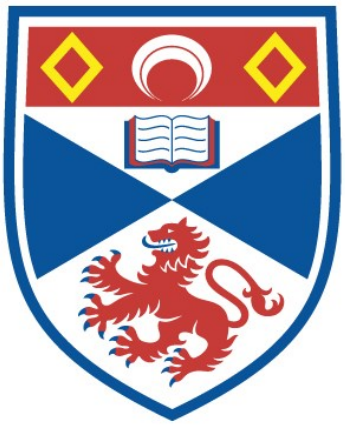
THE PYROLYSIS OF TRIPHENYLMETHANE, CARBAZOLE, AND TOLUENE

George Urquhart Ferguson

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE PYROLYSIS OF TRIPHENYLMETHANE, CARBAZOLE, AND TOLUENE.

being a Thesis presented by George Urquhart Ferguson to the University of St Andrews in application for the degree of Doctor of Philosophy.

August, 1956.

MS
1962

DECLARATION.

I hereby declare the following Thesis to be a record of results of experiments carried out by me, and furthermore that the Thesis is my own composition and has not been previously presented in application for a higher degree.

The investigations were carried out in the Chemistry Research Laboratories of the United College, University of St Andrews, under the direction of Doctor Charles Horrex.

C E R T I F I C A T E.

I hereby certify that Mr. George Urquhart Ferguson spent nine terms at research work under my direction, and that he has fulfilled the conditions of Ordinance No.16 (St. Andrews), and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Director of Research.

UNIVERSITY CAREER.

I entered the United College of the University of St. Andrews in October, 1948 and graduated with second class honours in Chemistry in July, 1952.

The research described in this Thesis was carried out in the United College under the direction of Doctor Charles Herrex between the period July, 1952 and October, 1954.

ACKNOWLEDGEMENTS.

The author wishes to express his gratitude to Dr. Charles Horrex for his invaluable assistance and advice on theoretical and practical aspects of the investigations detailed in this Thesis. He thanks Professor John Read, F.R.S. for the provision of facilities to carry out the research.

The author wishes to acknowledge the co-operation and helpful discussions with Mr.A.N.Hamer and Mr R.N. Pitillo, the assistance of Mr T.Norris in the construction of apparatus, and of Mr M.Zochowski in the preparation of compounds used in the work.

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Contents.

Summary.

1. Triphenyl Methane.

(a) The pyrolytic decomposition of this substance yielded 9-phenyl fluorene and hydrogen in equimolecular proportions. A hydrocarbon $C_{23}H_{18}$ was also produced in very small amount.

(b) The decomposition proceeded by a first order mechanism, obeying the rate equation $k=1.26 \times 10^{14} e^{-71,100/RT}$.

2. Carbazole.

(a) The thermal decomposition of this compound has been shown not to give the dimer 9:9' dicarbazyl under usual pyrolytic conditions,

(b) It is more probable that hydrogen and a phenazine type of compound are produced by the reaction of two carbazyl radicals.

(c) There appeared to be some heterogeneous decomposition on the walls of the reactor during carbazole pyrolysis and a carbon coated surface is necessary.

(d) The kinetic data obtained were rather scattered due to poor reproducibility, but first order rate constants are of a magnitude given by $k = 10^{13} e^{-75,000/RT}$.

(e) If the energy of activation is ascribed to the dissociation of the N-H link in the molecule, it is shown that the resonance energy of the radical is in rough agreement with expectations from other data.

3. Toluene.

(a) Since two values for the energy of activation of the primary decomposition of toluene have been reported, a brief re-examination of the problem has been made, using the nitrogen carrier gas technique.

(b) The value of 77.5 K.cals./mole found was in agreement with the previous work of Szwarc, and the products were those anticipated on the basis of his proposed mechanism.

(c) An examination is made of the papers by Szwarc[31] and Steacie.[40]

Introduction.

In the past 25 years there has been a continuous growth of interest taken in the kinetics of thermal decomposition of organic molecules. It has been recognised that many of these decompositions may proceed by the initial fission of a single bond leading to the production of free radicals which then function as intermediates in many secondary processes. Much attention has therefore been directed to the nature of these radicals, their general behaviour, and the kind of products to which they give rise.

It has been known for many years from early work by Rice that, under suitable experimental conditions, the energy of activation for the decomposition can be ascribed to the heat of dissociation of some critical bond in a molecule. Since all chemical reactions involve the making and breaking of bonds, a knowledge of bond strengths is fundamental to the understanding of many reaction mechanisms. In studying the kinetics of decompositions in an endeavour to obtain bond dissociation energies a variety of precautions has to be taken so that the mechanism of decomposition shall be as simple as possible and a series of products be avoided.

When the researches detailed in the following pages began, the author had available to him certain general techniques for following continuously the rates of thermal decompositions and had the aim of applying these to substances which were

expected to yield, as one of the products of primary decomposition radicals which would have a high degree of stability. It was felt that this property in itself should minimise unwanted secondary reactions.

Previous work done with the techniques included studies of the decompositions of diphenylmethane and fluorene[2] in an endeavour to find the strength of the weakest C-H bond in these substances and thereby provide an experimental check on a variety of theoretical calculations of the degree of resonance stabilisation in the radicals produced from these compounds. Experimental methods had been evolved for handling these involatile substances, and with suitable modifications were adapted in the present work to extend the investigations to the relatively similar compounds carbazole and triphenylmethane.

Theoretical calculations on the stabilities of the benzyl, diphenylmethyl, and triphenylmethyl[3] radicals had given for their resonance energies a graded series of values, 15, 27, and 38 kilogram calories respectively, and it was somewhat surprising to find from detailed studies of the pyrolysis of $PhCH_2-X$ compounds, particularly where $X=CH_3$, that the experimental resonance energy of the benzyl radical might be as high as 24 Kg. calories[4]. Reasons have been given for the discrepancy between the theoretical and experimental values for benzyl; the latter having sound support. It is, of course, of great interest to consider the change of resonance energy in the phenylated methyl radicals and, during the course of our work on triphenylmethane, a paper appeared in the literature attack-

:ing the experimental basis which ascribed 24 Kg.cals. as the resonance energy of the benzyl radical. Studies on the bromination of toluene also suggested that the side chain C-H bond had, in fact, a dissociation energy of 89.5[5] rather than 77.5 K.cals. These experimental discrepancies made it appear desirable to check the salient details of the toluene pyrolysis using our somehwat different techniques. A report on some experimental work on this topic is included in this thesis.

In all the studies reported in the subsequent sections a common method of approach has been followed. As a preliminary to the kinetic work, detailed investigations have been made of the precise nature and stoichiometry of the decompositions occurring. Since the conditions chosen for the work involve low concentrations of reactants as a means of minimising secondary processes, the analytical techniques to determine the precise stoichiometry have faced considerable difficulties peculiar to each case investigated. The general techniques of gas analysis, ultra violet spectrophotometry, mass spectrometry, and chromatography have been enlisted to solve the problems involved. Although many of these techniques have been common to all three substances, the problems were sufficiently individual to merit their discussion in separate sections.

Before proceeding to detail the experimental work of these

investigations a brief survey is given in the following pages of relevant knowledge in certain fields.

The Strength of Chemical Bonds.

It is customary to discriminate between two quantities in this field - the average bond energy (bond energy term), and the bond dissociation energy. The former is a quantity assigned to each of the bonds in a molecule so that the sum over all the bonds gives the heat of atomisation of the molecule. The idea originated in work of Fajans[6,7] and has been much used by Pauling.[8] In the development of this idea it had to be assumed that the value for a particular bond was constant in different molecules and independent of molecular environment. This is so contrary to chemical experience concerning the reactivity of the same type of link in different environments that it is clearly only a working approximation. It does, however, enable values to be produced which are useful for broad comparison.

An example of the deduction of the average bond energy of the H-S bond[9] from thermochemical data is as follows:-

$H_2S + 1\frac{1}{2}O_2 \longrightarrow SO_2 + H_2O + 134.5$ K.cals.

$SO_2 \longrightarrow S$ (rhombic) $+ O_2 -$ 70.91 K.cals

S (rhombic) $\longrightarrow S(^3p) -$ 66.3 K.cals.

$H_2O(l) \longrightarrow H_2 + \frac{1}{2}O_2 -$ 68.32 K.cals.

$H_2 \longrightarrow 2H -$ 104.1 K.cals.

By addition $H_2S \longrightarrow S(^3p) + 2H -$ 175. K.cals.

Thus 2 H-S bonds are ruptured by 175.1 K.cals.so the average bond

energy of the H-S bond is taken to be 87.5 K.cals/mole.

Taking the general case of a molecule containing n bonds of the same kind, then if Q is the heat of formation of the molecule from gaseous atoms, we have

$q = Q/n$, where q is the average bond energy.

This process is satisfactory for treatment of such molecules where the energy must necessarily be proportioned equally among the n identical bonds. The method can be applied to molecules with more than 1 type of bond, thus for CH_3Cl, if we know q(C-H) from study of methane and can assess $q(CH_3-Cl)$, then,

$q(C-Cl) = q(CH_3-Cl) - 3q(C-H)$. It must necessarily be assumed that the value of q(C-H) is the same in CH_3Cl and in CH_4.

The concept of an average bond energy meets other difficulties in its definition and evaluation. When speaking about the heats of atomisation of molecules the precise states of the dissociated atoms have to be specified. Normally the ground states are taken but the "valence states" might be more satisfying on logical grounds. From the practical point of view the average bond energies in carbon compounds are subject to an uncertainty in the value to be taken for the latent heat of atomisation of carbon, L_c. In the case of methane the equations:

$CH_4 \longrightarrow C_{(s)} + 2H_2$ - 17. 865 K.cals.

$C_{(s)} \longrightarrow C_{(g)}$ - L_c.

$2H_2 \longrightarrow 4H$ - 208.2

lead to the final equation:

$CH_4 \longrightarrow C_{(g)} + 4H - L_c - 226.065$ K.cals. and an accurate value for D(C-H) depends upon an accurate value for L_c.

This question has been discussed at length in recent years without a definite result emerging. Consistent schemes of average bond energies merely require that one value shall be adhered to in all calculations. Since the present investigations have not been concerned with average bond energies, no further discussion of these matters seems appropriate and some techniques for obtaining more important bond dissociation energies are summarised in the following paragraphs.

Relevant Experimental Techniques for Bond Energy Determinations.

All the methods for determining bond dissociation energies involve supplying energy to molecules. This energy can be thermal energy, light energy, or the energy derived from bombardment of the molecules by electron impact.

Spectroscopic Methods.

This method is applicable in particular to diatomic molecules, the reactions being of the type;

$$X_2 + h\nu \longrightarrow X + X$$

or, more often:

$X_2 + h\nu \longrightarrow X + X^{*}$ where X^{*} represents an electronically excited atom. The energy $X \rightarrow X^{*}$ must be known and hence the method is inapplicable to the case of complex

molecules which possess a complex spectrum due to the large variety of possible electronic, vibrational, and rotational excitation mechanisms.

The energy required for the decomposition, $h\nu$, can be estimated either by observation of the onset of the continuum with possible uncertainty of the knowledge of the process; or by extrapolation of the vibrational energy terms.

Thermal Energy.

In this method, heat is applied to increase the energy of the molecules, and, according to circumstances, either an equilibrium dissociation or a rate of dissociation is studied.

Equilibrium method: The primary step in a decomposition which would yield useful data must take the form:

$$R_1 - R_2 \rightleftharpoons R_1- + -R_2$$

where R_1 and R_2 are unreactive entities.

Examples of this are the determinations of the C-C bond strengths in aryl ethanes, in particular that of hexaphenylethane by Ziegler and Ewald.[10,11]

$$Ph_3C - CPh_3 \rightleftharpoons 2PhCH_3$$

and the bond strength of the I_2 molecule[12]

$$I_2 \rightleftharpoons 2I$$

A method of observation of the extent of reaction is necessary, and the determinations of vapour pressures, molecular weights, pressure changes, and magnetic properties have been utilised. Where the bond strength is appreciable (10-15 K.cals.) /

the percentage decomposition is generally small at reasonable temperatures and pressures, and a further disadvantage of the method is that the radicals produced are generally reactive. If the equilibrium constant can be measured at various temperatures, then the heat of the reaction, which is, for the cases considered, the bond energy, may be determined by graphical adaptation of the equation:

$$d \ln K_{eq}/dT = \Delta H/RT^2$$

where K_{eq} = equilibrium constant.

T = absolute temperature.

ΔH = heat of reaction.

Kinetic Methods.

All kinetic methods of determining bond dissociation energies depend on the fact that the heat of a reaction at constant volume is equal to the difference of the energies of activation for the forward and reverse processes.

A general case is represented by Bodenstein's[13] work on hydrogen and bromine combination. In this the processes:

(f) $Br + H_2 \longrightarrow HBr + H$ $\quad E_f = 18$ K.cals.

(r) $H + HBr \longrightarrow H_2 + Br$ $\quad E_r = 1.3$ K.cals.

are known to play a part. The forward reaction is therefore 16.7 K.cals. endothermic and this must clearly be equal to the difference of the heats of dissociation of H_2 and HBr. When one of these is known, the other is calculable. In this case

both heats of dissociation are, of course, known from other sources but the same method has been applied with success to hydrocarbons by Kistiakowsky[14] using:

$$RH + Br \rightleftharpoons HBr + R\text{-}$$

and the same kind of reasoning to find the dissociation energy of R-H. The method requires an exhaustive study of the kinetics of a reaction in order to isolate values of activation energies for the particular atom molecule reactions and this has not been achieved in many cases.

A more frequent use of the equations $q = E_f - E_r$ occurs in the case of bond dissociation processes where the recombination process is assumed to have zero activation energy. There is experimental evidence[15,16,17] that this is the case for methyl radicals; it is certainly not the case, however, for triphenylmethyl radicals since it is known that the heat of dissociation of C_2PH_6 is 10 - 12 K.cals., while the energy of activation for the process is 18 - 20 K.cals.[10,11].

In order to make practical use of the idea that the energy of activation of a bond dissociation process can be equated to the heat of dissociation it has to be established that the experimental activation energy for the whole reaction as observed is that of the first step. A bond dissociation process inevitably produces free radicals (or a radical and an atom) and ideally we should estimate the rate of formation of these bodies. This is very rarely possible and techniques have been developed to trap the radicals by reaction with some

suitable substance. The early work of Paneth,[18] followed by that of Rice,[1] used metallic mirrors outside the reaction zone. This work has been summarised in many places and need not be detailed here. A more modern technique is to include an easily attacked compound in the homogeneous reaction mixture. Toluene has been extensively used in the pyrolysis of organic bromides[19,20] and with other substances such as hydrazine,[21] butene,[22] acetyl peroxide,[23] n-propyl benzene,[24] and n-butyl benzene.[25]

The use of toluene as a free radical or free atom acceptor is subject to certain limitations. It is obviously most suitable when it is itself stable at the temperature of the reaction under investigation. Since it decomposes more easily than most hydrocarbons it has a limited use with these compounds. The alkyl and aryl bromides, however, decompose more readily than the parent hydrocarbons, and typify cases where both the free radicals and atoms formed can be successfully reacted with toluene and so replaced by relatively inert benzyl radicals.

The general reaction scheme is on the following lines:

$$CH_3Br \longrightarrow CH_3\text{-} + Br\text{-}$$

$$CH_3\text{-} + PhCH_3 \longrightarrow CH_4 + PhCH_2\text{-}$$

$$Br\text{-} + PhCH_3 \longrightarrow HBr + PhCH_2\text{-}$$

$$2\ PhCH_2\text{-} \longrightarrow PhCH_2CH_2Ph$$

At lower temperatures there is evidence that toluene may not be sufficiently susceptible to free radical attack to ensure rapid removal of these entities.[26,27,28] Thus the attack by CH_3 radicals is estimated to have an activation energy of 7-11 K.cals.

In the case of the thermal decomposition of mercury dimethyl, which occurs at relatively low temperatures, the presence of toluene had no effect on the rate or the products.[29]

Used within its limitations the toluene radical acceptor technique has simplified many pyrolytic reactions, and provided the bulk of our knowledge of bond dissociation energies in organic molecules.

It is well known, of course, that when a radical acceptor is not present the decomposition of substances can be very complicated processes, particularly when chain sequences occur. The mechanisms suggested by Rice and Herzfeld[30] permit a kinetic analysis to be made in many cases but the details of their schemes often require quantitative verification.

A particular case of the radical acceptor technique, which is relevant to the work of this thesis occurs when the reactant acts as its own radical or free atom acceptor. The pyrolysis of toluene supplies an example of this type with the suggested scheme[31]:

$$PhCH_3 \longrightarrow PhCH_2\text{-} + \text{-}H$$

$$H + PhCH_3 \longrightarrow PhCH_2\text{-} + H_2$$

$$2PhCH_2\text{-} \longrightarrow PhCH_2 - CH_2Ph$$

Unfortunately the reaction must be more complicated than this since methane is also formed. It is said that this occurs by:

$PhCH_3 + H \longrightarrow CH_4 + \text{-}Ph$, but this will be discussed in a later section.

The obvious requirement for this type of inhibition of chain sequences is that the radical produced shall be relatively unreactive.

Electron impact method.

This technique involves the use of the mass spectrometer to identify and estimate the ions produced by the bombardment of molecules with electrons of known energy. The presence of ions is observed as a rise in the voltage of a particular mass. The sensitivity of the method depends on the difference between the appearance potential of the given ion produced by electron bombardment of either reactants or end products, and ionization potential of the free radical. It has been shown experimentally that excited molecules are not present in sufficient quantity to invalidate the assumption that free radicals are responsible for the changes in ion current.

The method has already extended tenfold the pressure range in which radicals are detectable, thus bridging the gap between mirror and spectroscopic methods so that low pressure combustion phenomena may be studied.

A molecule XY when bombarded with electrons of energy E, ionises and dissociates with a certain probability when $E \geq A(X^+)$ where $A(X^+)$ is the appearance potential of X^+. If atoms or radicals X are already present as a result of thermal or chemical dissociation of the molecule, then $E \geq I(X^+)$ gives X^+ where $I(X^+)$ is the ionization potential of the radical or atom X. $I(X^+)$

is less than $A(X^+)$ by an amount which depends on the dissociation energy of the parent molecule and the kinetic energies of the fragments. If the gas admitted to the mass spectrometer is believed to contain free radicals it is possible to select a value of the electron bombarding energy which is sufficient to produce the process $R- + \epsilon \rightarrow R^+ + 2\epsilon$, but not enough to bring about $RH + \epsilon \rightarrow R^+ + H + 2\epsilon$. In this way the positive ion current of a given mass in a mass spectrometer can measure the concentration of a given free radical.

In the determination of $D(CH_3 - H)$ in methane, Stevenson[32] used two variations of this technique. By bombardment of ethane molecules he measured the appearance potential of the ethyl radical, and from similar treatment of propane he produced methyl radicals. From these data, with the known heats of formation of ethane, propane and hydrogen, he was able to calculate $D(CH_3 - H)$.

$$C_3H_8 \longrightarrow C_2H_5^+ + CH_3 + \epsilon \qquad \Delta E = 14.50eV \ (i.e. = A(C_2H_5^+)$$

$$\epsilon + H + C_2H_5^+ \rightarrow C_2H_6 \qquad \Delta E = -15.20eV \ (i.e. = -A(C_2H_5^+)$$

$$C_2H_6 + CH_4 \longrightarrow C_3H_8 + 2H \qquad \Delta E = 5.08eV$$

by addition $CH_4 \longrightarrow CH_3 + H \qquad \Delta E = 4.38eV$

Hence $D(CH_3 - H) = 101 \pm 4.5$ K.cal.

Later Hipple and Stevenson[33] decomposed lead tetramethyl in a furnace attached to the ionization chamber of a mass spectrometer. As the furnace temperature rose the ion current due to mass 15 diminished and then rose at the same rate as that for mass 16. This showed that at the higher temperatures the

methyl radicals were being produced by decomposition of methane by electron impact.

The difference between the appearance potentials of CH_3 produced by the two processes gave $D(CH_3 - H)$.

$CH_3 \longrightarrow CH_3^+ + \epsilon$ $\quad I(CH_3^+) = 10.0$ eV.

$CH_4 \longrightarrow CH_3^+ + H + \epsilon$ $\quad A(CH_3^+) = 14.44$ eV.

By subtraction: $CH_4 \longrightarrow CH_3 + H$ $\quad E = 4.44$ eV.

The two values are in very good agreement,

Mass Spectrometry.

The dissociation of molecules under electron impact has been used in the work of this thesis as a method of analysis and it seems appropriate at this stage to outline some of the features of this procedure.

The mass spectrometer used in the investigations to be detailed in this thesis was constructed from the design of Nier.[34] Essentially the instrument comprises a source of high energy electrons which collide with molecules introduced to the ionization chamber in a path perpendicular to the electron beam. Since the instrument operates under very high vacuum, the molecules are allowed to enter the chamber through a molecular leak, the high pressure side being at a few millimetres of mercury. The ions produced by the bombardment are drawn out of the ionization box, focussed, and then accelerated through a potential of about 2000 volts. They then pass into a tube which is bent through 120°.

A sector shaped magnetic field is applied at the bend and the deviation of the ion beam is inversely proportional to its mass. This sorts the initial beam of particles out into beams with definite charge to mass ratio, and by varying the strength of the magnetic field these beams are brought in turn on to an insulated electrode.

This "collector plate" is fitted at the lower end of the tube, connected to earth through a high value grid resister. Electrons flow from earth to neutralise the charge on the ions reaching the collector plate, and the resulting neutral atoms are removed from the system by an efficient pumping unit. The voltage developed across the resistor is fed into a direct current amplifier, using 100% negative feed-back and the out-put is displayed on an automatic voltage recorder which has a pen as its indicator, tracing out a line on a moving chart. Thus a "trace" is obtained as the magnet current control is altered and from the location of the peaks shown in the trace, an assessment of the composition and concentration of the entering molecule may be made.

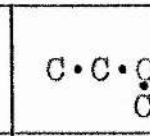
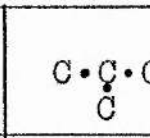
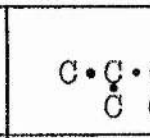
Let the ion have a charge e and the accelerating voltage be V. The kinetic energy acquired by the ion may then be expressed as follows:-

$$\text{Kinetic energy} = \tfrac{1}{2}mv^2 = Ve \qquad (1)$$

where m is the mass of the ion and v the velocity it acquires. When the ion reaches the magnetic field, there is an interaction and the radius of the curve it traverses, r, may be expressed

Table 1.

Relative Abundances of Ions from the Trimethylpentanes.

Mass			
114	0.1	0.02	0.3
99	3.0	5.0	0.1
85	3.0	0.02	0.05
71	1.0	1.0	40.0
57	70.0	80.0	9.0
43	15.0	20.0	80.0

in terms of its velocity v, and the magnetic field H.

$$Hev = \frac{mv^2}{r} \qquad (2)$$

by combining equations (1) and (2)

$$e/m = 2V/H^2r^2$$

r is fixed for a given instrument and hence only the ions travelling with velocity **v** will follow this path, thus e/m is fixed for a given V and a given H. Generally one is kept constant (V) and the other is varied so that the ion current due to each value of e/m is recorded in sequence.

With electrons of energy due to 70 - 100 Volts acceleration the "cracking pattern" includes a wide variety of fragments and the proportions are characteristic of the parent substance. In illustration we cite the data for trimethyl pentanes.[35]

Principles of analysis by mass spectrometer.

When the mass spectrum of a mixture is obtained it will be a composite mass spectrum and it can be considered as being a summation or superposition of the mass spectra of all the components of the mixture. The analysis of the mixture consists of unravelling the mixture spectrum. All the peaks recorded are not necessarily needed and some can be used as checks of the mass numbers, or of the whole analysis from the point of calculation errors, instrumental errors, or failure to take account of one or more of the constituents of the mixture. The spectrum of every component of the mixture must be known.

Methods of analysis.

Direct method.

In the complete direct method, calibrations of critical components of a mixture are made and computations are carried through at a large number of masses in order to obtain a check on the accuracy of the analysis as well as to discover unexpected constituents.

Comparison method.

A synthetic mixture of the components of the unknown mixture is prepared. Between analyses of the unknown mixture, samples of the synthetic mixture are introduced into the instrument so that a periodic check is made of sensitivity. This is the better of the two methods, and is the method employed whenever possible in the present work.

Application of the mass spectrometer to problems in chemical kinetics.

In the branch of kinetics most closely associated with the work detailed in this thesis, the continuous flow technique is the method most conveniently adapted to the determination of bond energies. The applicability of the mass spectrometer to gas analyses has already been dealt with, and if the inlet leak to a mass spectrometer could be installed within a circulating system then the experimenter has an ideal means of following the reaction being investigated.

Since a considerable proportion of time has to be spent in preparing a circulating system for pyrolytic work, having a method of analysing products continuously allows a great deal of work to be done when the analyses necessary to obtain data may be carried out in a relatively short time. In addition, since a prerequisite of much work is steady conditions, then a series of experiments may be done without opening up the system to the atmosphere, a procedure which is necessary when material has to be abstracted from the system in order to have it analysed by alternative methods.

The mass spectrometer has been used in kinetic studies of the pyrolysis of ethane and deutero-ethane by Wall and Moore[36], in the reaction of methane and deuterium on nickel by Kemball[37], and in the investigation of states of catalyst in the reaction between methane and deuteromethane on nickel by Wright and Taylor[38], to cite a few examples.

What appears to have been the first investigation of a reaction basically similar to the current work was the pyrolysis of diborane by Bragg, McCarty, and Norton[39]. The reactant was contained in a thermostatted Pyrex bulb fitted with a leak to a mass spectrometer. Having previously drawn up relationships between the voltages and partial pressures for each of the products of the reaction, it was possible to fully elucidate the mechanism of the decomposition in terms of B_2H_2, B_4H_{10}, B_5H_9, B_5H_{11}, $B_{10}H_{14}$. Argon was used to check the sensitivity of the instrument. The pyrolysis was

repeated using the pressure rise as a measure of decomposition, and the results obtained in this way were considered as being higher in precision than those obtained mass-spectrometrically. This view is shared by Blades and Steacie[38] in the pyrolysis of toluene.

This criticism is undoubtedly justified in these two cases since the workers did only one or two experiments at each temperature, and attempted to draw conclusions from about 20 runs. There is a scatter in results obtained by this technique but if a large number of runs is done and the best result at each particular temperature is selected mathematically then the criticism is invalidated, and full use may be made of what is a most elegant method.

TRIPHENYLMETHANE.

Pyrolysis of Triphenylmethane.

The pyrolytic study of the phenylated methanes was commenced by Szwarc[31] who obtained a value of 77.5 K.cals/mole for the strength of the side-chain carbon-hydrogen bond in toluene molecule. The decomposition of this substance has been re-investigated by Steacie[40], and this will be discussed in a later section of this thesis.

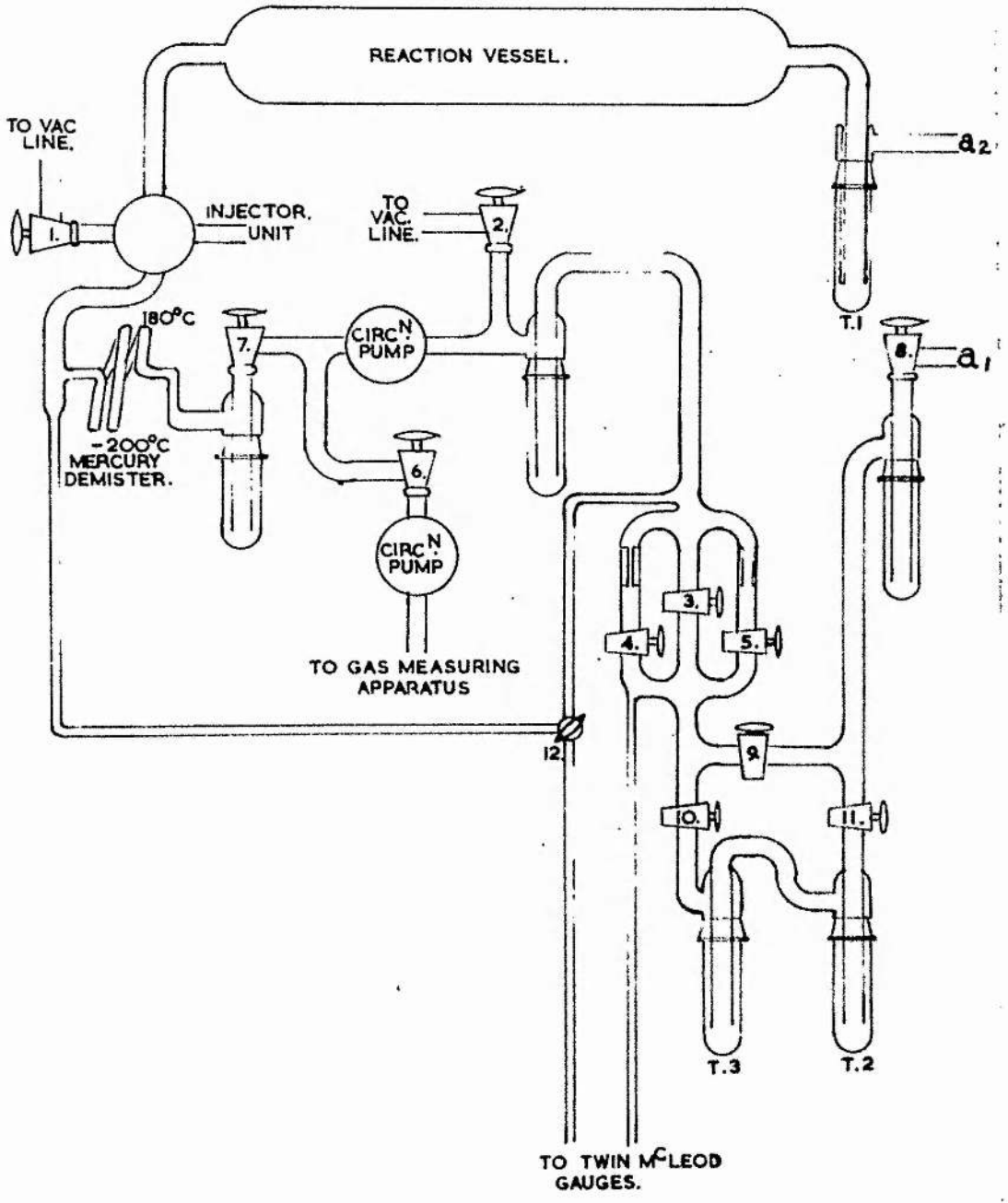
In work on the pyrolysis of diphenylmethane, McCrae[2] found the products of the reaction to be in agreement with those reported by Graebe[41], namely fluorene and hydrogen, but in addition detected small amounts of tetraphenyl ethylene. It was suggested that the formation of fluorene, the principal product, was a result of the loss of one of the methylenic hydrogen atoms of diphenylmethane followed by closure of the 5-membered ring and migration of a hydrogen atom. The loss of the primary hydrogen atom was shown to follow a first order kinetic law.

Ipatiev and Dolgof[42] reported that triphenylmethane at 300°C yielded very small amounts of 9-phenyl-fluorene and hydrogen, and Hurd[43] showed that triphenylmethyl chloride on pyrolysis yielded 9-phenyl-fluorene and hydrogen chloride. Hurd and Mold[7] showed that at 700°C triphenylmethyl chloride gave up to 26% of triphenylmethyl which, subsequently, formed the more stable fluorene.

The present investigation was carried out to ascertain

DIAGRAM 1.

APPARATUS FOR PYROLYSES.



whether this reaction was kinetically of the first order, and, if so, to assess the C-H bond strength. By using a heat of formation of the triphenylmethyl radical derived from work on hexaphenylethane Szwarc[45] has calculated that this value should be 75 K.cals/mole.

The technique employed in the investigation was to transport the reactant through a reaction vessel by a carrier gas in a circulating system, collect and measure the reaction products. This method has been developed from the work of Butler and Polanyi[46] in their investigations on organic halides.

The apparatus.

Diagram 1. shows the arrangement of the circulating system. The carrier gas, nitrogen, conveyed the starting material from the exit of the injector system to the reaction vessel, then, having deposited solid products in trap T.1 passed through a purifying system, and continued back to the injector.

Vacuum system.

The system was evacuated by means of a mercury vapour pump backed by a Metropolitan-Vickers two stage rotary oil pump. When using a liquid air trap between the apparatus and the pumping unit a pressure of 10^{-6} cms. of mercury could be attained with this system.

Reaction vessel

The/

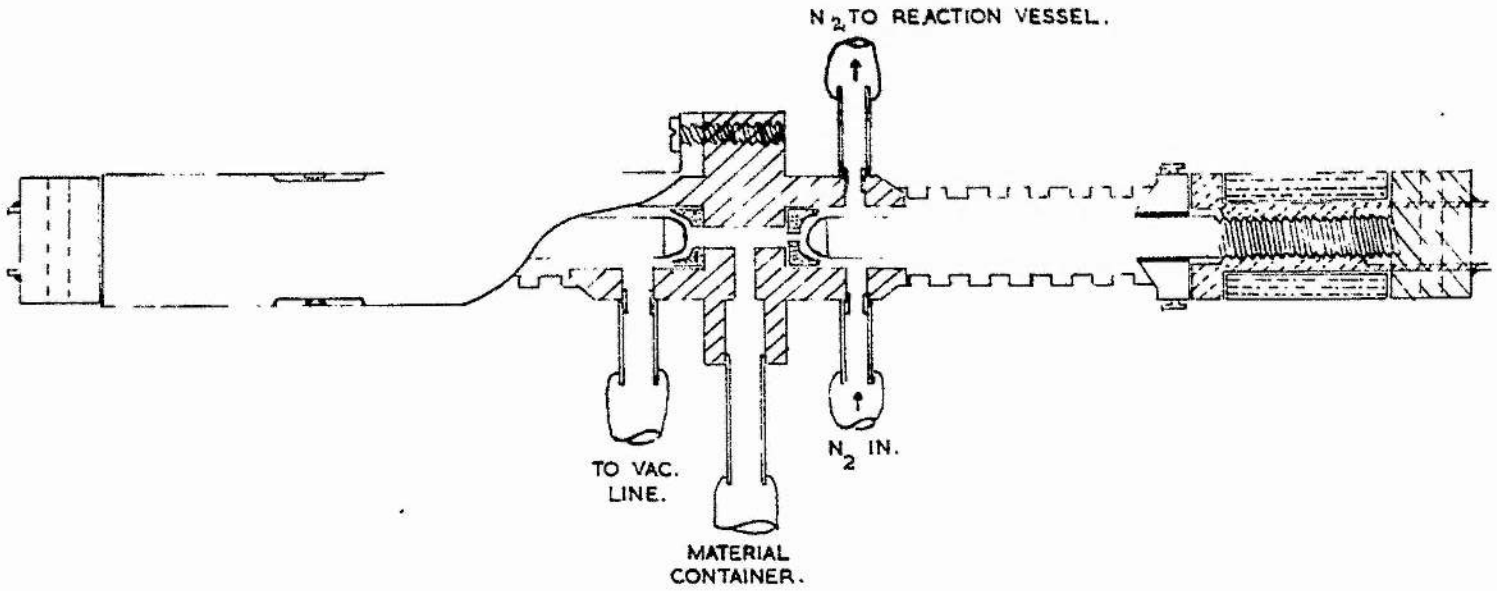
The reaction vessel consisted of a silica tube of internal diameter 2.9 cms. and of length 70 cms. The ends of the vessel were fused to 12 mm. silica tube, and the connections to the circulating system were by two "Jencons" Pyrex/Silica graded seals. Initially the connection of the vessel to the system had been by B.19 silica cones engaging in Pyrex sockets, but the temperature at which the leads had to be maintained was so high that no lubricant remained undecomposed.

Furnace.

A piece of 2½" internal diameter inconel tubing, 65 cms. in length was covered with asbestos paper. On this a layer of alundum cement, ¼" thick was deposited. After drying, the element of nichrome tape was wound on, there being two turns per cm. length for the first and last 10 cms. of the furnace and one turn per cm. over the rest of the furnace. Tapping points were made on the element 10, 25, 40, and 55 cms. along the furnace so that shunt resistors could be put across each section and be adjusted to compensate for unequal heat losses along the whole furnace. Each shunt was a 100 ohm rheostat rated to carry 4 amps. The nichrome tape was further covered by a ¼" layer of alundum, the whole being contained inside a length of 3" internal diameter asbestos pipe lagging. In the latter part of the investigations it was found necessary to fit a length of 5" pipe lagging in order to be able to

DIAGRAM 2

INJECTOR UNIT.



operate the reaction vessel at 900°C.

The supply of electricity to the heating element was controlled by having two 110 volt "Variac" auto transformers fed from a 220 volt constant voltage transformer operated from the mains supply. The temperature could be varied easily by manual adjustment of the output of the auto transformers, and the constancy of the temperature was a result of the constancy of the voltage.

The temperature of the reaction vessel was measured by a chromel-alumel thermocouple fitted inside a narrow bore silica tube which lay alongside the reaction vessel inside the furnace. The milli voltage of the thermocouple was determined by a Pye potentiometer, the conversion to temperature being made from data of Roeser, Dahl, and Gowens[47].

Injector system.

Diagram 2. shows the construction of the injector system. Since the vapour pressures of both carbazol and triphenylmethane are so low, an injector system had to be devised which could be operated at temperatures up to and above 300°C. This requirement immediately precluded the use of gaskets of materials such as "Teflon", and consequently a design of valve was evolved which was entirely silver soldered at all joints.

The/

The body of the valve was turned from a piece of 2" diameter mild steel rod, 2" in length. All but the central ½" was turned down to 1" diameter and the rod was drilled through with a ⅛" drill. ⅛" at each end was turned to provide a tapering shoulder on which to fit stainless steel bellows. The central hole was next enlarged to ⅝" along all but the central ½" and into each end there was fitted a small copper seat, previously ground to be an accurate fitting for a ⅝" diameter stainless steel ball. These two seats were bedded into molten silver solder. The left hand seat was drilled to ⅛" and the right hand one with a hole 0.012" in diameter. On the right hand side a hole, ¼" diameter, was drilled diametrically to allow the carrier gas to pass through, and to facilitate this an annular groove ⅛" deep was turned on the inside of the valve body, thus ensuring that there would be no pressure drop across the valve. On the left hand side provision was made for one lead to the vacuum line to allow of quick evacuation of the injector and material container.

The stainless steel balls were next soldered to ⅝" diameter stainless steel rod, the other ends of the rods being cut with a ⅝" British Standards Fine thread. Thus rotation of a similarly threaded guide caused the ball and rod to move along their axis. The fixed guide was held in position by means of an outer copper tube (not shown in the diagram) which was fixed by a flange to the faces of

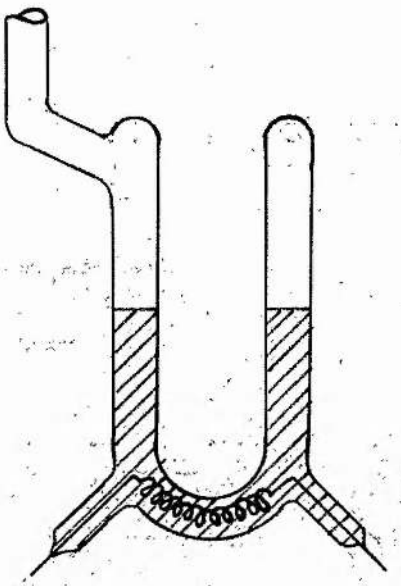
the central body with four O.B.A. screws. Slots were cut in the outer body and in these the heads of screws ran; these screws were fixed in the brass shoulder pieces to which the other ends of the bellows were soldered. There was thus no possibility of the bellows suffering twisting as a result of the valve being operated. At each end of the valve a mild steel cylinder was turned to fit over the threaded socket of the rod and the two pieces were soldered together. This cylinder held a similar cylinder which was free and to which were attached the two mounting rods for the whole assembly.

Connections to the circulating system and vacuum line were by means of Nilo K/Pyrex graded seals; the seals were soldered to small steel adaptors which, in turn, were soldered to the side arms of the valve body.

A glass container of starting material was attached by a similar seal to the central part of the valve body, access being made to the capillary by an $\frac{1}{8}$" hole drilled in the body to meet the axial $\frac{1}{8}$" hole. Thus, on withdrawing the right hand ball from the copper seat, material could flow through the copper capillary and be carried by the circulating gas to the reaction vessel. The entire valve system was covered with asbestos paper on which was wound a nichrome element, this being covered by asbestos rope.

Container Heater.

The flow of starting material to the circulating system depends on the pressure of vapour inside the container, so the container has to be maintained at a constant temperature. The construction of the heater is shown in the accompanying sketch. It consists of a Dewar-like vessel fitted with a heating element in the space between the two surfaces. An air reflux condenser is fused to the ring seal and nichrome tape is wound over the outside to maintain the temperature of the vapour from the boiling liquid.



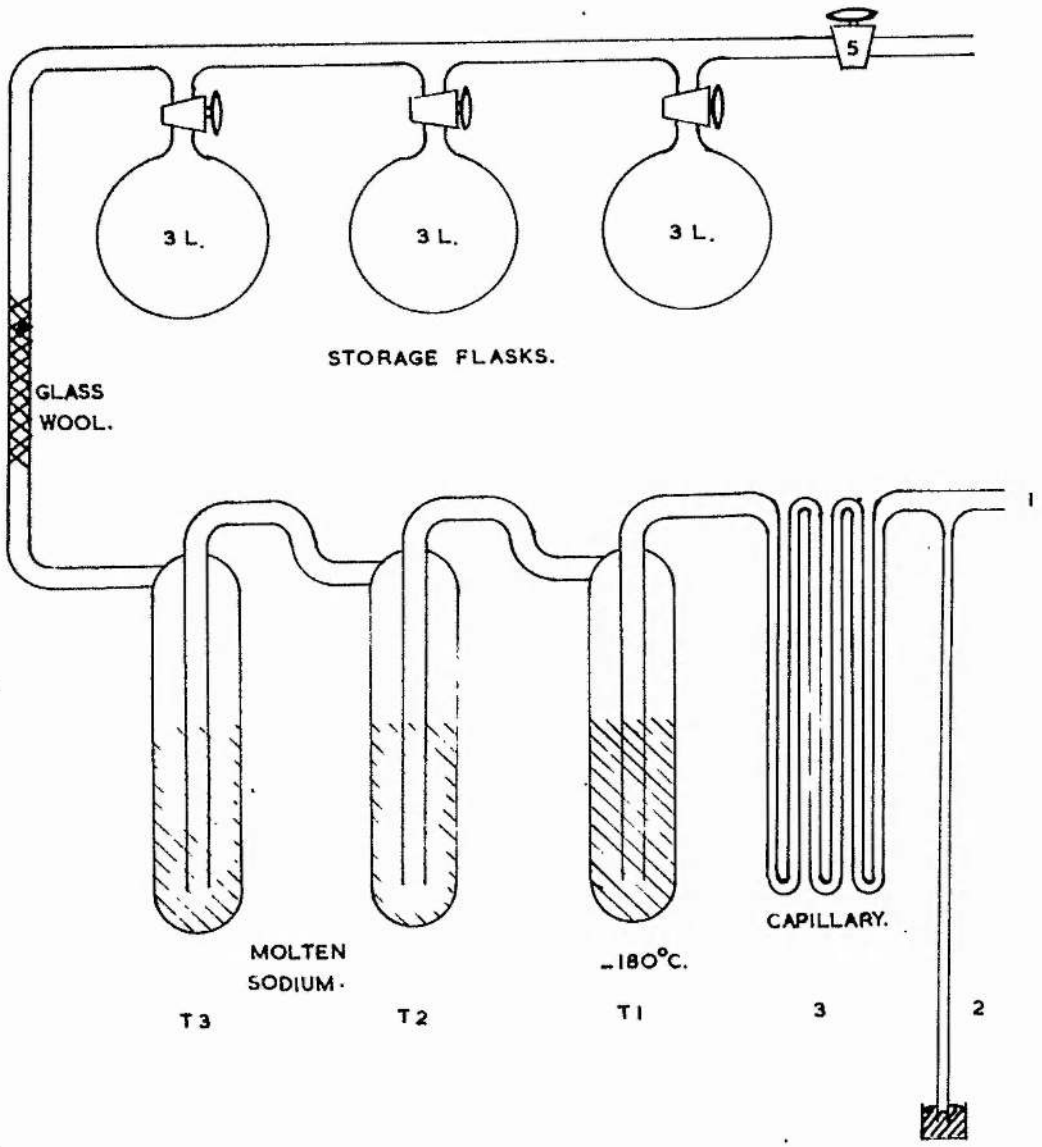
Container heater.

By knowing the vapour pressure data for the compounds being investigated, it was possible to choose the heating liquid to give the desired vapour pressures.

Variations in atmospheric pressure from day to day resulted in a number of degrees difference in boiling point of the liquids, and since the temperature/vapour pressure curve of triphenylmethane is steep, it was found necessary to use a manostat in conjunction with the container heater. This then ensured steady delivery

DIAGRAM 3

NITROGEN PURIFICATION SYSTEM.



from the valve irrespective of outside factors.

Circulating pump.

Circulation of the carrier gas was by means of a three jet mercury diffusion pump. This was heated in an iron pot containing tin/lead alloy, the pot being wound with a nichrome wire element and sitting on a hotplate. The current to both the hotplate and the pot was supplied through a "Sunvic" energy regulator which maintained the temperature of the bath to within 2°C.

The body of the pump itself was heated by a nichrome element.

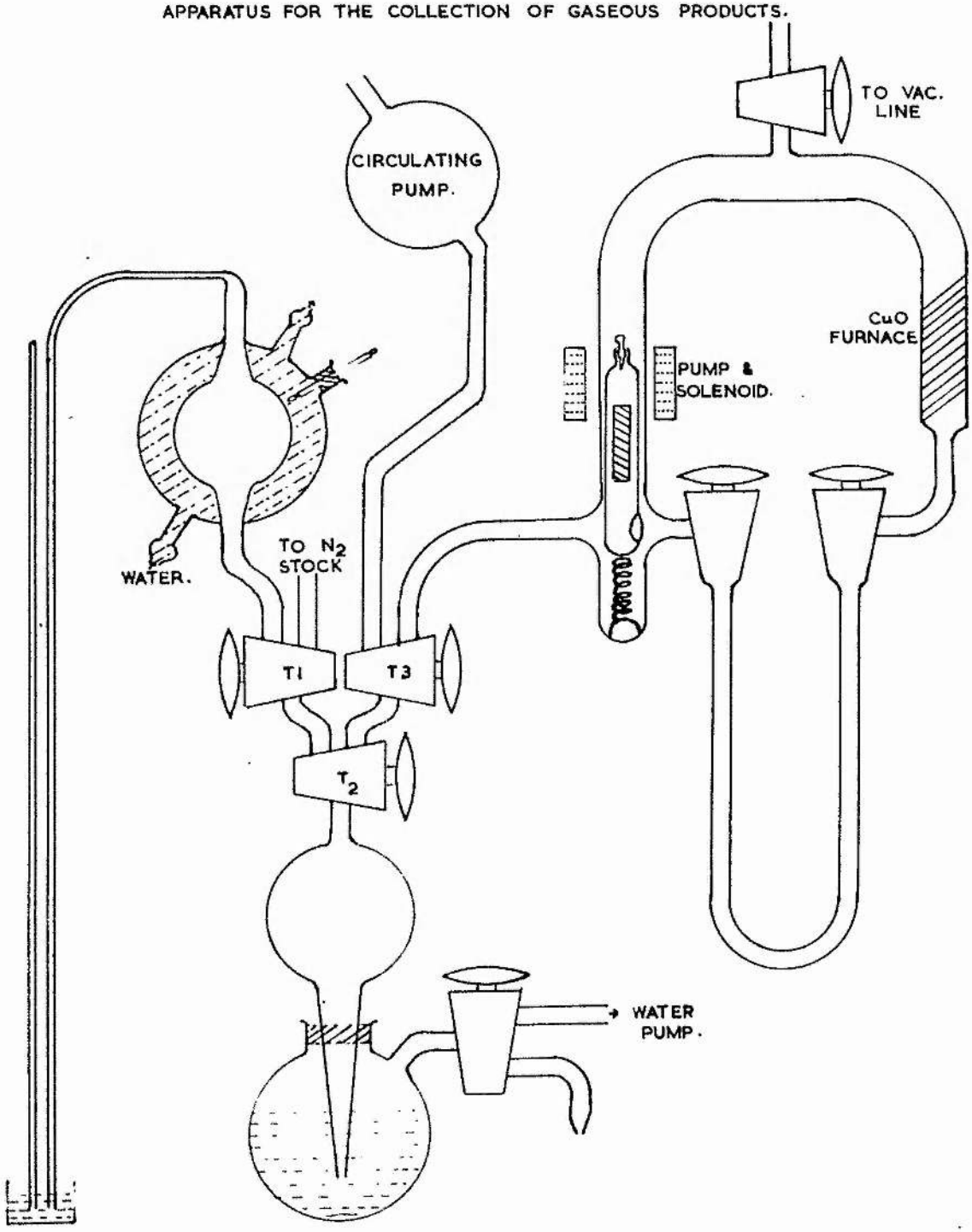
A second circulating pump was fitted to the apparatus to be used in series with the main circulating pump when the gaseous products of a run were to be collected, since it was found that one pump was insufficient to evacuate the system to 10^{-6} cms. Hg. This second pump, when required, was simply heated with a Bunsen burner as maximum speed of pumping, rather than constancy, was the primary requirement.

Nitrogen Purification System.

Diagram 3. shows the apparatus which was used to remove impurities from the commercial product. The gas entered the system at 1 and the flow was adjusted so that the pressure was just greater than 1 atmosphere by allowing bubbles to escape slowly from manometer (2). The gas then flowed very slowly through the long capillary (3)

DIAGRAM 4.

APPARATUS FOR THE COLLECTION OF GASEOUS PRODUCTS.



into a liquid air trap (T.1), then through two traps (T.2 and T.3) containing metallic sodium at 300°C. Any sodium peroxide formed was removed by the glass wool filter (4). From this point the pure nitrogen was fed to 3 storage flasks, each of 3 litre capacity, whence it was transferred to the apparatus by means of the tap (5).

Gas measuring system.

The apparatus shown on diagram 4 was used for the introduction to the apparatus of a known amount of carrier gas, and after the run for collecting all the gases in the system. Thus, by difference, the amount of gas formed in the run could be measured.

The orifice of tap T.1 was connected to the tap (5) of diagram 3. facing page 29 . By operation of the Toepler pump N_2 was drawn through taps T.1 and T.2 into the bulb of the pump, then by turning T.1 through 180° it was transferred to the water-jacketed reservoir connected to the manometer. The manometer was selected to be of the same diameter as the barometer alongside to compensate for capillary effect. After thermal equilibrium had been established, the pressure of the gas was measured. It was then transferred via the Toepler and tap T.3, through circulating pump C.P.2 to the circulating system. The pressure of the gas left in the reservoir was again noted and hence the amount of gas in the system was known.

At/

At the conclusion of a run, all gases were collected in the reservoir by a procedure similar to the above. After equilibrating, the pressure was noted. Any hydrogen formed was estimated by burning in a hot copper oxide furnace. The gases in the reservoir were transferred through T.3 to the combustion apparatus.

This consisted of a small electro magnetic pump, the solenoid of which was energised intermittently, 30 times per minute, by having a cam operated switch driven by a geared motor. This caused the iron cored piston to rise, and when the energising supply was broken it fell back on its supporting springs. Thus the gases in the system were circulated over the copper oxide furnace, through the U tube, cooled in liquid air to retain any water formed, and back to the furnace. Operation of this system for 10 minutes sufficed to remove the hydrogen formed in one run. The residual nitrogen, and any other incombustible gases present were pumped back to the reservoir and measured.

This system was used to check results obtained on the mass spectrometer, and also when the mass spectrometer was required for other work being conducted in the department.

Pressure measurements made on the system could readily be reduced to 273°A and hence were convertible to gram moles.

A/

A typical calculation was as follows:-

Run 2.

	Barometer cms.	Reservoir cms.	Temp.	p_{273} cms.
Initial N_2	74.7	51.9	16.7°	21.52
After run	74.7	50.08	19.0°	23.02
After CuO 1.	74.7	51.76	18.0°	21.52
After CuO 2.	74.7	51.76	18.0°	21.52

Thus pressure due to H_2 1.5 cms. Hg.

Volume of bulb 144 mls.

Moles of hydrogen 13.0×10^{-5}.

Flow Capillaries.

Diagram 1 facing page 23 of the complete apparatus had two flow capillaries operated by taps 4 and 5. Tap 3 opened a by-pass, used when an unimpeded flow of gas was required, such as when the products of a run were being driven into the measuring system or when the apparatus was being pumped out. The flow capillaries were two pieces of Pyrex capillary tubing of different bores and of which all the dimensions were very accurately known. Twin Mc Leod gauges were situated across the capillary in use and so the pressure drop due to the passage of the gas was obtained. By application of the capillary constant the rate of flow in moles per second was calculated.

The capillary constant was obtained by application of Poiseuille's relationship which governs non-turbulent flow of liquids and gases:-

$$\text{Vol/sec.} = \pi p\, r^4 / 8\eta l.$$

This equation has been modified by Meyer to govern the flow of gases and reads:-

$$\text{Rate of flow (moles/sec)} = \pi r^4 (p_1^2 - p_2^2)/16\eta l\, R\, T$$

where r = radius of tube in cms.
l = length of tube in cms.
p_1 and p_2 = pressure at ends of capillary.
η = viscosity of gas in poises.
R = gas constant.
T = temperature (^oA).

Thus, assuming room temperature constant, it may be taken that:-

Rate of flow $= K (p_1^2 - p_2^2)$, where K is the capillary constant.

Previous work in the department had established by experiment that the calculated K for the particular capillaries used was in reasonable agreement with the values obtained by passing a known volume of gas through the capillaries in a given time and measuring the pressure drop due to the flow.

Collection of Solid Products.

At various times different devices were employed for the collection of the solid products of the runs. A series of U tubes cooled to different temperatures was employed on the preliminary runs with each material as a device for roughly fractionating the products.

In the early work on triphenylmethane, three traps were fitted in series, the first being surrounded by an electrically heated jacket at 100°C, the second by a beaker of water at 50°C, while the third was kept in liquid air.

After the nature of the products had been established, the most convenient type of trap was the one represented in diagram 1. which was fitted with an internal electrically heated sleeve, which ensured that the products would collect right at the bottom of the trap.

Having abstracted the solid products, the points a_1, a_2 on the diagram were either joined with glass tubing if analysis of the gaseous products was to be made on the Gas Measuring System, or they were attached to the leads which, in turn, were attached to the mass spectrometer handling system.

The Mass Spectrometer.

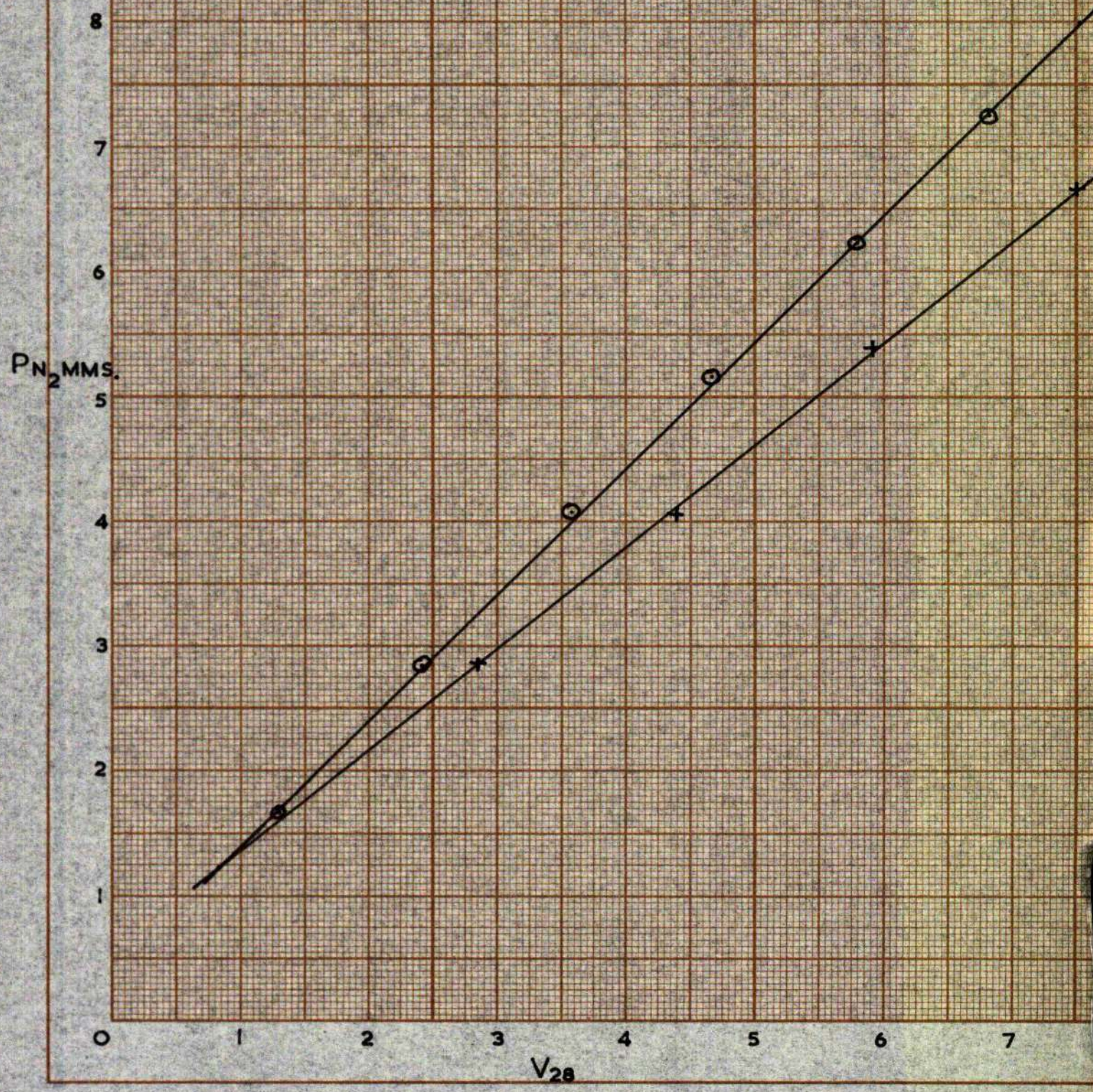
In the introduction to this thesis there is noted the fact that the instrument lends itself admirably to the continuous analysis of gaseous products of reactions.

The mass spectrometer available was fitted with a porous leak between the lead to the ionisation chamber and the gas circulation system used in the kinetic studies. This leak was of grade 4 F. "Metrosil" (a silicon carbide composition with small pore size) which was chosen to give reasonable linearity between pressure of gas on one side of it and the ions finally produced from that quantity which leaked into the mass spectrometer.

GRAPH I

RELATION BETWEEN PRESSURE OF N_2 AT LEAK AND V_{28}.

GRAPHS RELATE TO DIFFERENT DAYS

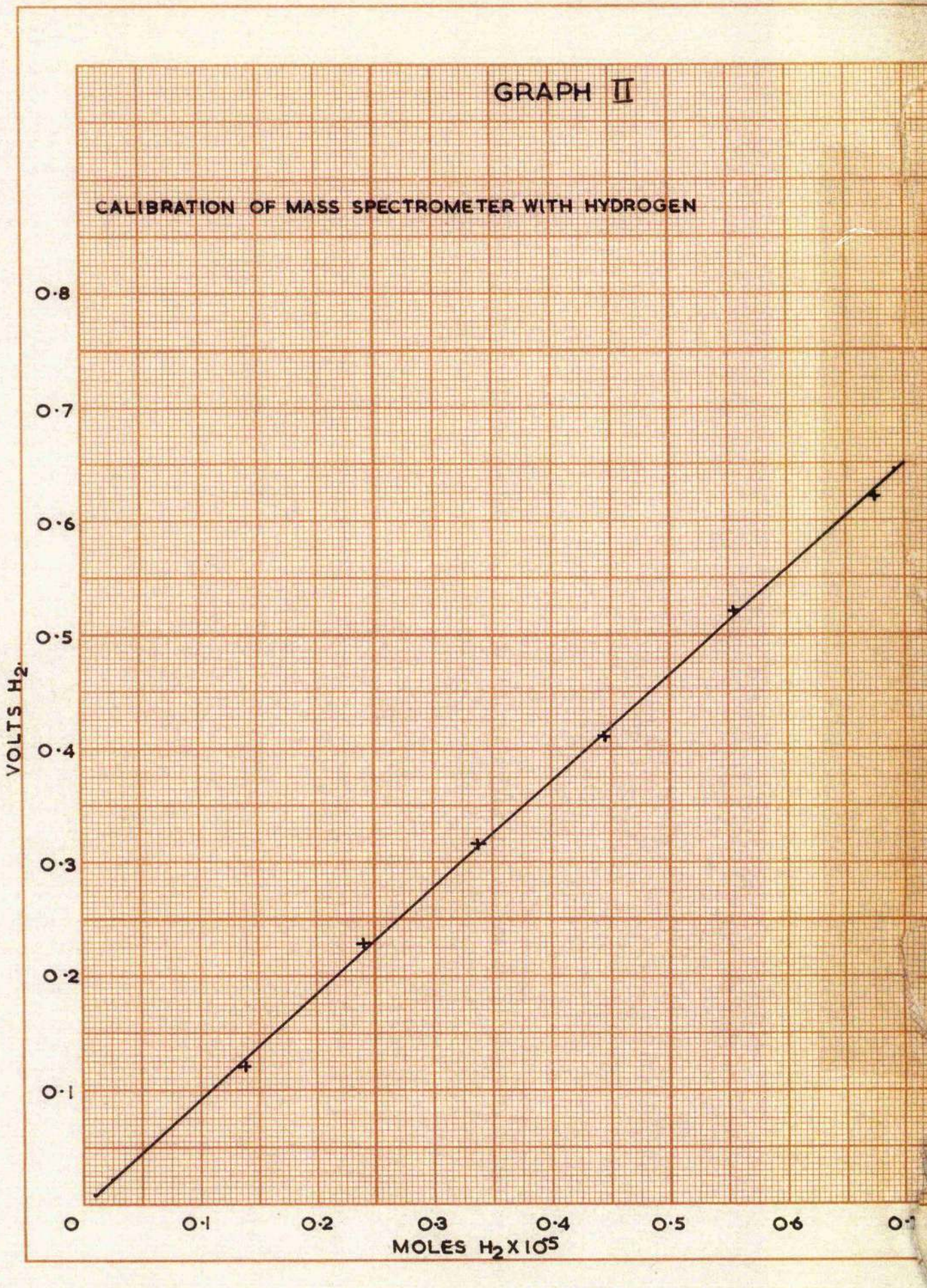


The pressure required for the circulation system was 3 to 5 mm. mercury and this was too high for the conventional "molecular leak" of Honig, but the pore size in the grade of "Metrosil" used enables the same effect to be achieved in spite of the higher pressures. That this is true is borne out by graph I where pressure of nitrogen at the "Metrosil" leak is plotted against voltage recorded for mass 28 peak.

Two lines are drawn, obtained on different days, The sensitivity of the instrument varies from day to day and before it can be used as an analytical tool, a way must be found of dealing with this variation of sensitivity. If we relate pressure of nitrogen and voltage recorded in the form:-

$$p_{N2} = \alpha V_{N_2}$$

where V_{N2} is the voltage of the mass 28 peak, and α is the gradient of the line obtained by plotting data of pressure and voltage, then an α is obtained for each day. This is very readily done. Since this sensitivity effect is applicable to all materials, it can be allowed for by multiplying all observed voltages by α , the 'sensitivity factor' obtained from nitrogen and so data may be accumulated over a period of days consistently. This, in fact, is what must be done. Calibration of the instrument was effected


GRAPH II
CALIBRATION OF MASS SPECTROMETER WITH HYDROGEN
VOLTS H_2
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
0·1
0·2
0·3
0·4
0·5
0·6
MOLES $H_2 \times 10^5$

by introducing known amounts of hydrogen into the system and multiplying the observed voltage by the sensitivity factor. The latter was derived from an observation of the mass 28 peak voltage and the pressure at the leak made immediately after the observations on hydrogen. Thus graphs of moles of gas could be plotted against 'corrected' voltages of the given mass. Such a graph, graph II is the calibration curve for the instrument on hydrogen.

In actual runs the technique adopted was as follows:-

(a) before the run, the pressure at the leak and the voltages for m/e = 2 and 28 were observed.

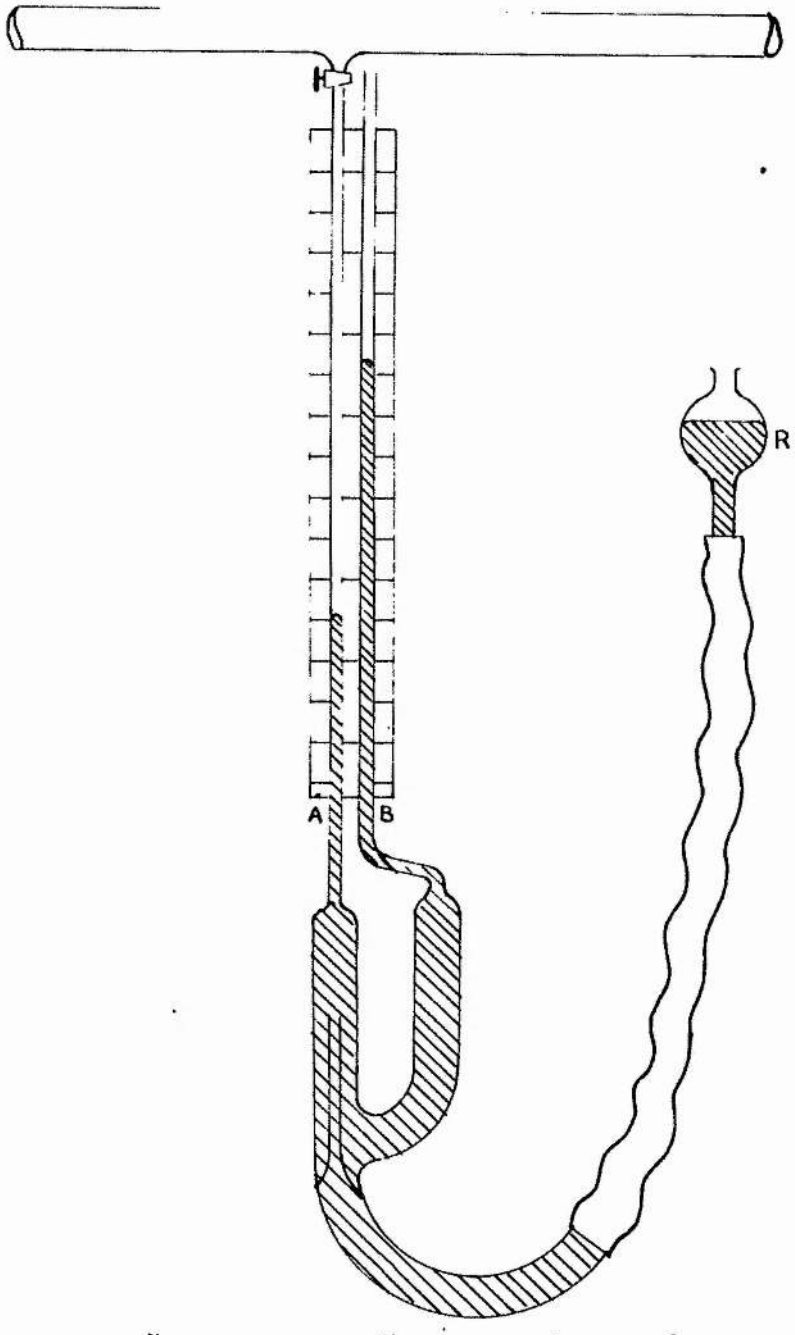
(b) after the run, (a) was repeated.

The difference between the corrected voltages of hydrogen in (a) and (b), by reference to the calibration graph, was then converted directly to moles of hydrogen.

In the derivation of the relation between recorded voltage and pressure of gas, the assumption was made that the number of electrons leaving the filament was a constant value. This is measured as "trap current" and has to be maintained constant in any mass spectrometer used for analysis. Sometimes this is done automatically but in the machine used it was the total electron emission from the filament which was stabilised. As a result a

DIAGRAM 5.

GAS BURETTE FOR H_2.



manual adjustment of "trap current" was made before every reading.

Gas Burette for calibration of Mass Spectrometer.

In order to inject known amounts of hydrogen into the mass spectrometer, a gas burette was constructed. The device is illustrated on diagram 5. 'A' was a carefully calibrated tube and 'B' a piece of similar tubing. To one end of A a straight through tap was fitted and the other end of A and one end of B were fitted to the mercury feed attached to reservoir R. Since in the attachment of the tap to A the bore of the top part of the tube had been changed, the volume of the irregular part of the tube was determined separately. It was found by calculation, that at 25°C the burette would deliver 3.03×10^{-6} moles of gas per centimetre displacement of mercury, and the volume of the end space at the same temperature would deliver 27.0×10^{-6} moles.

Attachment of the Pyrolysis Apparatus to the Mass Spectrometer.

It has been mentioned previously (page 34) that material was introduced to the mass spectrometer by a "Metrosil" leak. The gases circulating in the apparatus were passed over this leak and the leads for the gases were through two taps and over a system of three mercury cut-offs. A by-pass was also fitted to the system so that the pyrolysis apparatus could function as a circulating unit without the mass spectrometer.

DIAGRAM 6

MASS SPECTROMETER HANDLING SYSTEM.

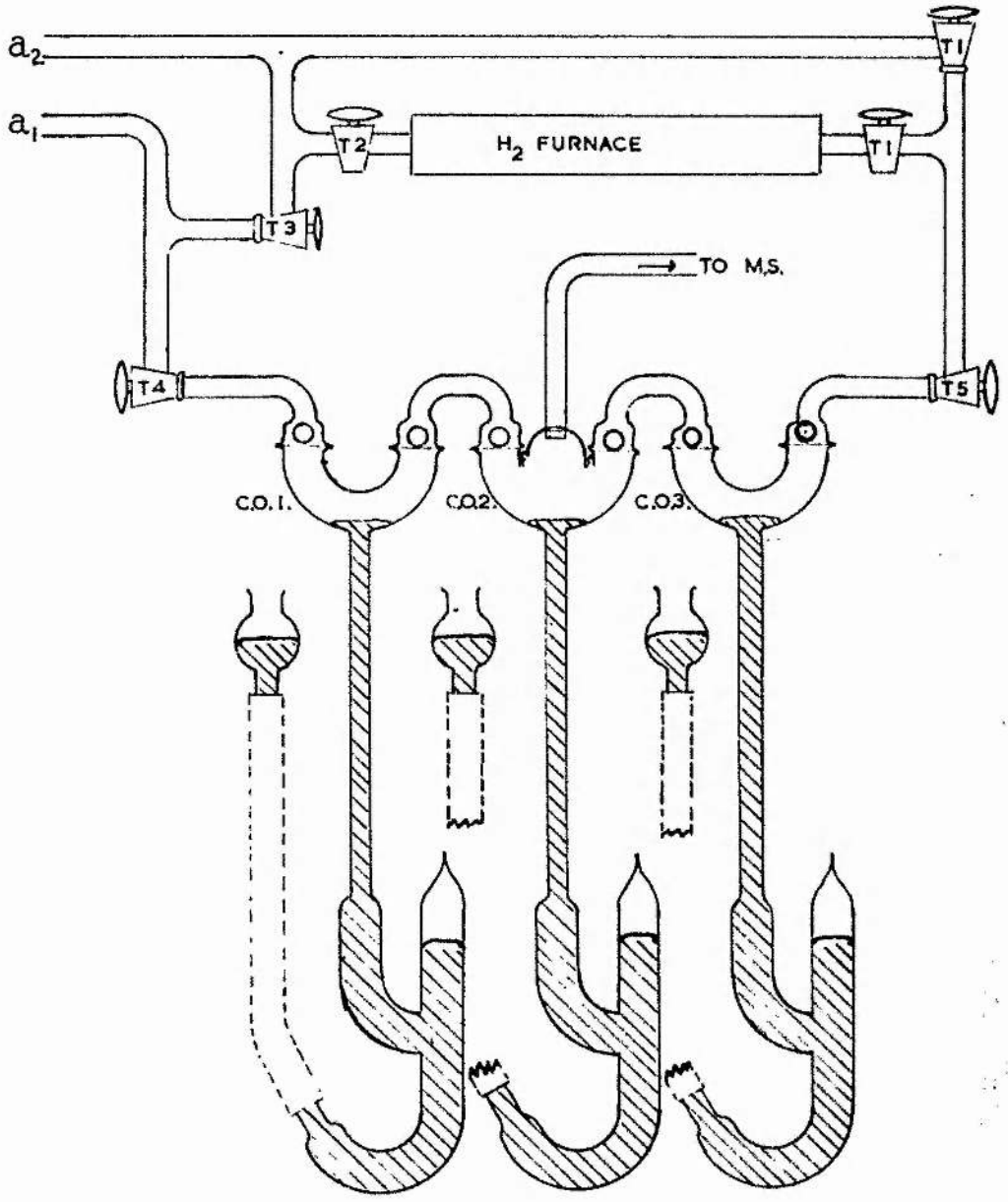


Diagram 6. shows the layout of the system which was constructed. Leads a_1 and a_2 were attached to the corresponding points on diagram 1. From a_1 the gases passed through tap T4, cut-off C.O.1, to C.O.2 in which the leak was fitted. From C.O.2 the gases then passed through tap T5 after going through C.O.3. From T5 two alternative paths were available, either a direct lead to a_2 and so back to the pyrolysis apparatus, or, when it was desired to reduce the amount of hydrogen in the system, through a long copper oxide furnace by opening T2 and turning 3 - way tap T1 so that the straight through tube was closed and access was made to the furnace.

Each cut-off was constructed in the following manner. Two pieces of 12mm. Pyrex tubing were thickened at one point and a $\frac{5}{8}$" ball attached to a long rod was rotated inside each of the thickened portions while the glass was soft, so forming a roughly shaped seat. After cooling the glass, the rod and ball was rotated slowly in a lathe and using carborundum powder, grades 80, 320, and 800 in turn, with glycerol, the seats were accurately shaped. When the grinding was completed, mercury was prevented from passing between the ball and seat on the application of a pressure of one atmosphere. Two side arms were next blown to each lead of the cut-off. These were of narrow bore glass and were for the ultimate inclusion of a piece of tungsten wire to restrict the travel of the ball betweem the wire

and the seat to approximately 1 cm.

The two pieces were then joined in a U and to the lowest part of the U a long piece of 5 mm. tubing was attached. The cut-off was completed by fitting a mercury seal, attached to a mercury reservoir by a length of rubber tubing. Taps T.4 and T.5 were simply to provide a rapid means of isolating the mass spectrometer should a sudden leak develop in the apparatus, and so protect the filament.

Tap T.3 completed the circulation path of the pyrolysis equipment when the mass spectrometer was not available for the analyses.

Operation of the Apparatus.

Before starting an experiment heaters on the injector, the inlet and outlet leads to the reaction vessel, and the mercury demister were switched on. The injector system was pumped through tap 1 to a pressure of 10^{-6} cms. of Hg and was then shut off. The container heater was switched on to let the material come to its definite vapour pressure while the rest of the apparatus was being prepared. The gas measuring system was then pumped down and a convenient amount of nitrogen was transferred from the storage system to the gas reservoir and allowed to come to thermal equilibrium.

The bulk of the apparatus was next evacuated through

tap 2 and had to be capable of holding a pressure of 10^{-6} cms. of Hg with the pumping system shut off before any work was started. When this condition was attained, liquid air or other suitable coolant was placed round the traps, the circulating pump was started, and tap 2 was closed.

The nitrogen was introduced to the apparatus through tap 6 which was then closed. The capillary by-pass was shut by tap 3 and a suitable capillary chosen by closing the tap of the other.

Taps 10 and 11, leading to a sodium trap and liquid air used for freeing the circulating gas from traces of oxygen, were closed and 9 left open. After opening the taps and cut-offs of the mass spectrometer, the by-pass was closed and the system was at the stage where material could be introduced to the reaction vessel.

After the run the capillary by-pass 3 was opened to facilitate pumping down of the system, tap 7 was shut, circulating pump 2 was started and the gases were collected in the reservoir for measurement, as described under the section 'Gas Measuring System' (page 30).

Calibration of the mass spectrometer.

The technique for the calibration of the mass spectrometer, with hydrogen, in the first case, was by the introduction of definite quantities of hydrogen from the gas burette into the circulating gas.

Referring to diagram 5 , the apparatus was evacuated with the burette tap open. All but the vacuum line and the burette were shut off from the pumping system. Hydrogen was introduced to the vacuum line from a cylinder to give 1 atmosphere and the burette was then rinsed with the gas. The system was then pumped down and the procedure repeated three times before the burette was filled and the tap closed. For the purpose of this work the hydrogen available in cylinders (99.5%) was sufficiently pure.

The apparatus was then filled with carrier gas in the normal way, and hydrogen was injected in small amounts, the voltage being noted on the mass spectrometer recorder after thorough mixing. It was found by observation of the recorded hydrogen voltage that the establishment of a homogeneous mixture of hydrogen and nitrogen required eight minutes from the time of the injection of the hydrogen. Graph II shows the result obtained from this experiment, and from it the sensitivity of the instrument is shown to be 10.75×10^{-5} moles per 'corrected' volt.

The figure had to be modified whenever the size of the pyrolysis apparatus was altered, since the injection of a given amount of hydrogen to a changed volume resulted in an alteration of peak height.

Table 2.

Optical Densities of 0.05 N K_2CrO_4.

λ.	Optical Density	$\epsilon_{exp} \times 10^{-3}$	$\epsilon_{lit} \times 10^{-3}$
254	0.333	2.74	2.57
265	0.416	3.42	3.16
280	0.429	3.53	3.29
289	0.273	2.24	2.08
297	0.125	1.03	0.93
303	0.058	0.47	0.498
313	0.027	0.222	0.193
334	0.127	1.04	0.985
366	0.57	4.69	4.416
405	0.157	1.29	1.328
436	0.042	0.345	0.313

Preparation of materials and compilation of Standard U.V.Data.

All analyses of solid products were made by examination of solutions in methanol or other solvent on a 'Unicam' Quartz Spectrophotometer. To attain proficiency in the use of the instrument, and, in one instance, to clear up some doubt as to the consistency of the readings on the instrument, a standard solution of 0.05 N potassium chromate in 0.05 N potassium hydroxide was prepared. The chromate used had been previously dried to constant weight. A curve was plotted of wavelength against optical density and compared with the standard data quoted by Weissberger[48] from figures in Landolt Bornstein. The data are given in table 2 and they show that the figures obtained differ to varying extents from the published values. A second and third solution of chromate were made up and results agreeing exactly with the first curve were obtained. The difference between the two sets of values must therefore be attributed to the fact that different types of instrument were being used, (the instrument in the department being a more modern type) or to differences in the purity of the calibrating substance. Other such differences were observed on consulting the literature not only in epsilon values, but also in the wavelengths of peaks themselves resulting from improvements in instrument design and technique. "The agreement between

different instruments is not as good as that between replicate readings on any one instrument, and each instrument should, for very accurate work, be calibrated against a standard substance"[49] . The consistency of the instrument should also be periodically checked[50] .

The particular instrument used suffered from lack of stability, and the main cause of this was traced to there being a very poor design of range switch which was also the 'on/off' switch. This switch was a paxolin Yaxley type of switch, and, through having to actually switch the instrument power off and on, a fine layer of worn metal was deposited on the moving poles. This had to be cleaned off periodically, and, in fact, due to the very hard work which this machine was called upon to do, two new switches had to be fitted during the period that this work was being done.

A second cause of the trouble was the galvanometer itself. The original movement was not enclosed and lack of consistent readings was finally traced to there being a very tiny piece of grit lodged in the bearings of the needle. The manufacturers acknowledged this fault by replacing it with a fully enclosed movement. While waiting for the replacement meter a lamp and scale system was set up temporarily and,using this apparatus, it was found that the accuracy to which one could work was within ½%, this

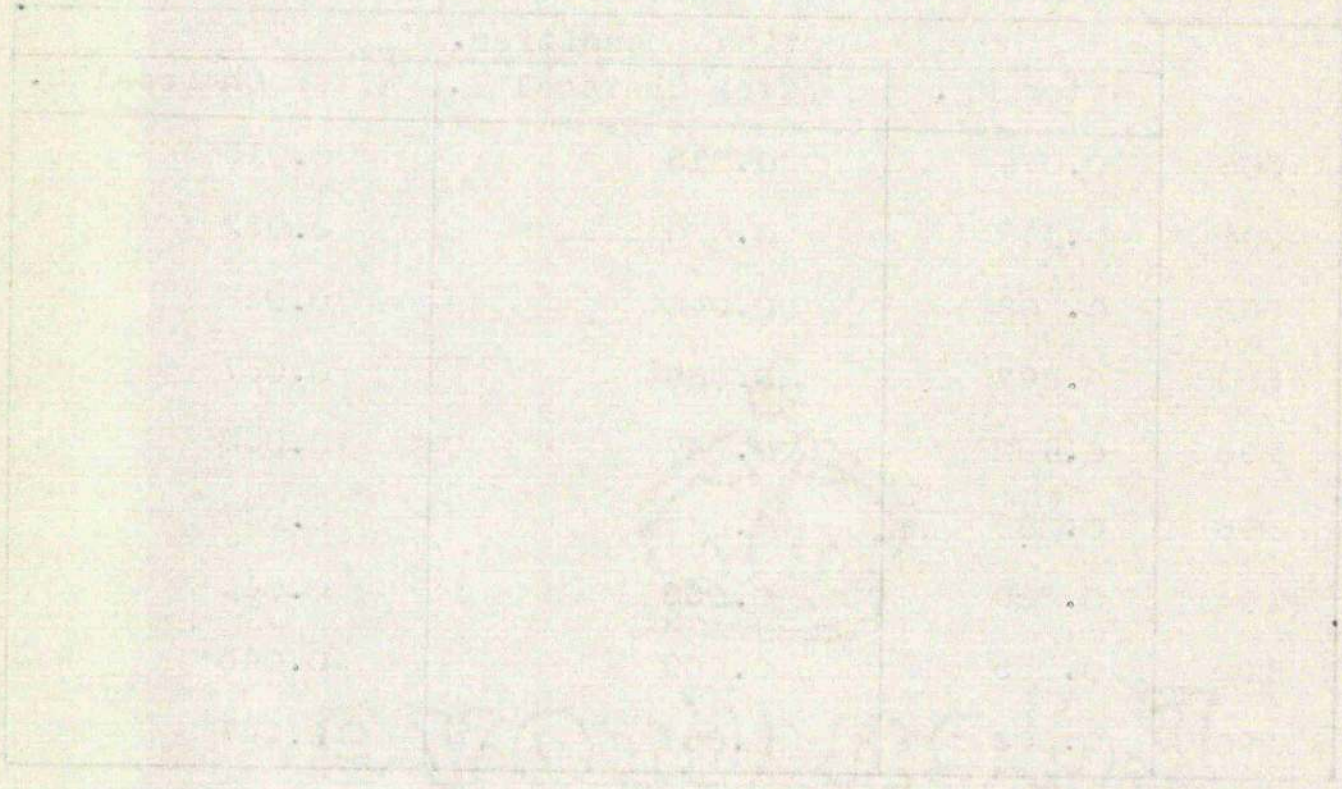


Table 3.

Purification of Methanol.

	Optical Densities.		
	After Mg.	After Charcoal 1.	After Charcoal 2.
306	0.074	0.015	0.015
304	0.118	0.020	0.032
302	0.308	0.046	0.038
300	0.592	0.089	0.037
298	0.422	0.067	0.032
296	0.288	0.045	0.037
294	0.329	0.058	0.043
292	0.355	0.069	0.043
290	0.378	0.067	0.047

being in contrast with the manufacturer's claim for 2%.

The solvent generally used was methanol. Commercial methanol was originally subjected to purification by distillation over Grignard grade of magnesium filings. On one occasion a poor batch of alcohol was received having low transmittancy at the low wavelength region of the spectrum. As a result of various experiments it was found that activated powdered charcoal would remove the impurities, whereas the magnesium only brought about a partial purification. Accordingly the treatment with magnesium was discontinued in favour of treatment with charcoal, and in fact, it was found later that due to a considerable improvement in the quality of the alcohol, the commercial variety was sometimes satisfactory without purification. Table 3 illustrates the improvement in a sample of magnesium treated methanol after two separate distillations from charcoal.

The apparatus used for making up the solutions to be examined, and for their dilutions was all carefully calibrated before use.

The solutions of the materials were made up by weighing a container of the material, after degassing in the melted state and cooling, on a micro balance. The necessary quantity of material was transferred to a flask, and the container was reweighed.

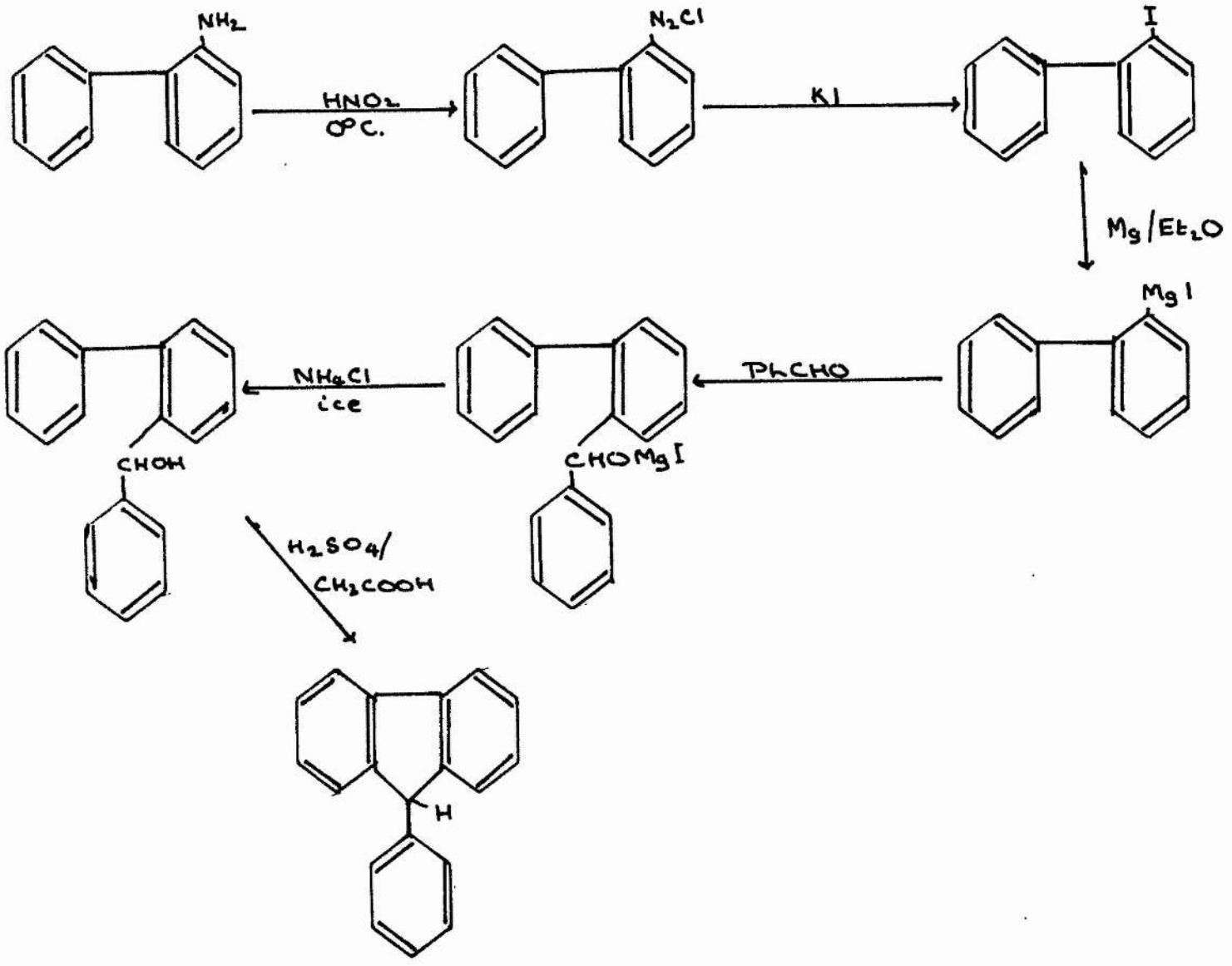
Preparation of triphenylmethane.

The method reported by Norris[51] was used. A stock of benzene was dried over sodium, and of carbon tetrachloride over calcium chloride. 292 gms. benzene and 116 gms. carbon tetrachloride were placed in a dry flask and 160 gms. aluminium chloride added. A reflux condenser was fitted and the flask immersed up to the neck in ice. After standing for two days 110 gms. of dry ether were added in small portions with shaking. The resulting reaction was quite vigorous, and cooling was necessary. After standing for a further two days the product was extracted in benzene, the solution washed with warm water, and the benzene evaporated. The product was vacuum distilled, and the fraction boiling at 190° - 215° C was collected. This material was purified by two crystallisations from methyl alcohol. The melting point was 88°C and a solution in methanol was examined by the spectrophotometer. The peak at 269 mμ was very much lower than that given in curves in the literature.[52,53] The material was redistilled and recrystallised when the melting point rose to 92°C and the 269 mμ peak increased. A check was then made of the temperature at which the bulk of the material distilled under 14 mm. pressure. It was found to be around 200°C. A curious point about the U.V. curve was that absorption was observed in the

anthracene region up to 350 mu. More critical examination of the absorption maxima and consultation of the literature showed that these peaks were, in fact, due to 9-phenyl anthracene. This impurity was finally removed by constructing a small electrically heated fractionating column which maintained the temperature at 190°C. By very slow distillation in this apparatus and then recrystallisation, a product was obtained free from any spurious absorption, but with the 269 mu peak still lower than that in the literature. The technique of fractional freezing was next adopted. A flask of triphenylmethane was placed in an electrically heated water bath and the temperature raised to 95°C. It was maintained there for half an hour, then lowered to 93°C. After remaining at that temperature for one hour, all liquid was decanted and the residual solid material twice recrystallised from alcohol. This product melted at 94°C and was perfectly pure triphenylmethane.

Leonard[54] found that triphenylmethane, which had been prepared by the Freidel Crafts reaction from benzene and chloroform, contained impurities which were evident in the U.V. spectrum and which were removed by crystallisation from ethyl alcohol. Hartley[55], in confirmation of this stated that the impurities were two in number, one being triphenylmethyl, which is yellow and apparently undergoes oxidation to triphenylmethyl peroxide.

DIAGRAM 7.



SYNTHESIS OF 9-PHENYL FLUORENE.

Preparation of 9-phenyl fluorene.

Since it was known that this compound was the product of the pyrolytic reaction, a quantity of the material was prepared in order that standard U.V. absorption curves might be constructed for spectrophotometric analysis.

The method of preparation was, fundamentally, a series of well known syntheses adapted to produce this particular substance. It is represented in the form of equations on the opposite page.

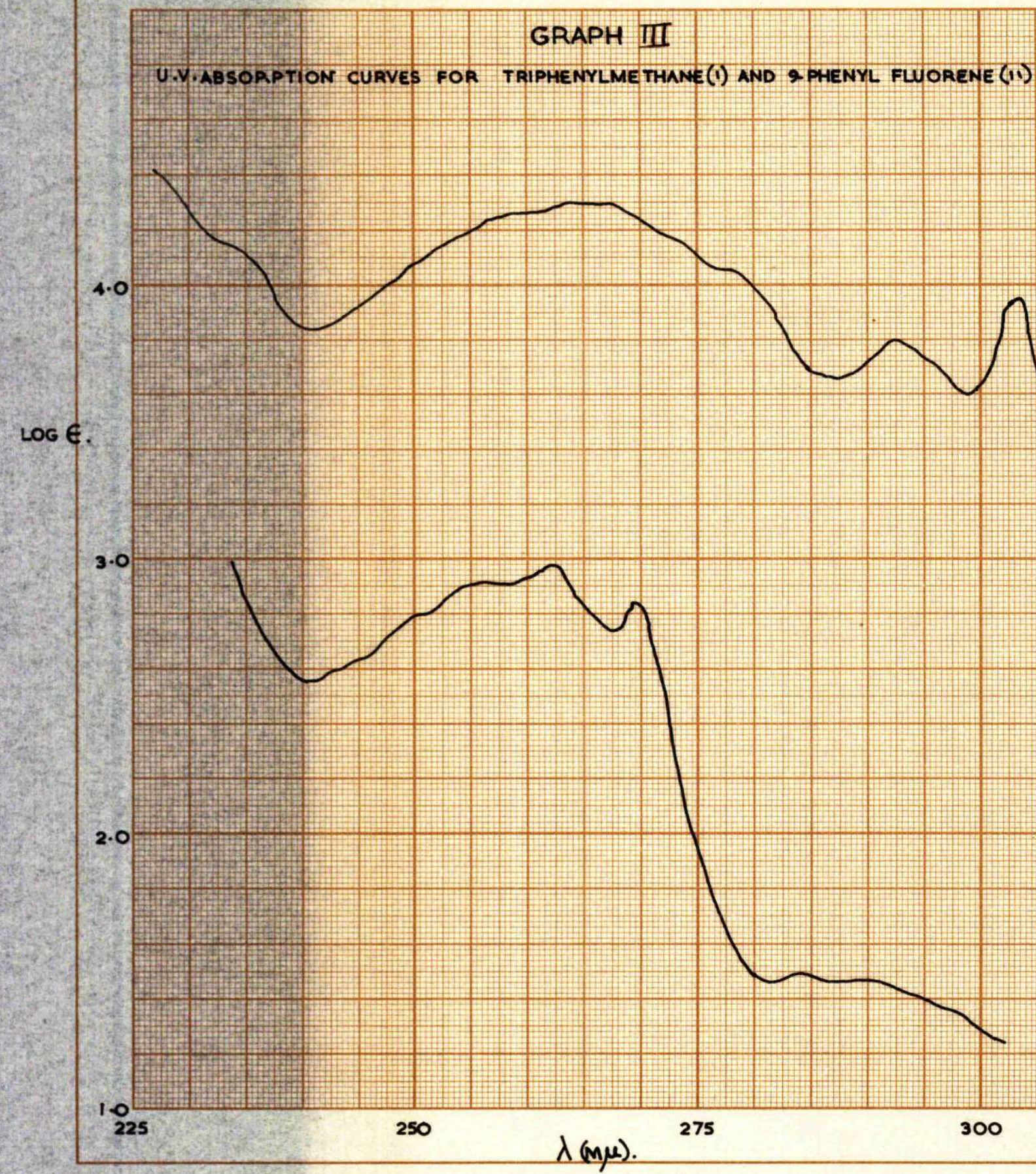
25 gms. of commercial o-amino diphenyl in approximately 400 mls. water was acidified with drops of concentrated hydrochloric acid. Adopting the normal temperature restriction for the operations of diazotisation, 2 N sodium nitrite was added with mechanical stirring till excess was present. A clear yellow solution of the diazo compound was thus obtained.

To this solution, 20 gms. of potassium iodide was added, giving a dark red coloration. The solution was then put on the water bath until evolution of nitrogen had ceased. After washing with sodium bisulphite, 43 gms. of an oil was separated and vacuum distilled, the fraction boiling between 158° and 160°C at 12 mms. being collected.

This oil was converted to the magnesium iodide complex by the normal Grignard technique. 16 gms. of benzaldehyde was added, yielding a yellow oil. This was separated, cooled

GRAPH III

U.V. ABSORPTION CURVES FOR TRIPHENYLMETHANE (I) AND 9-PHENYL FLUORENE (II)



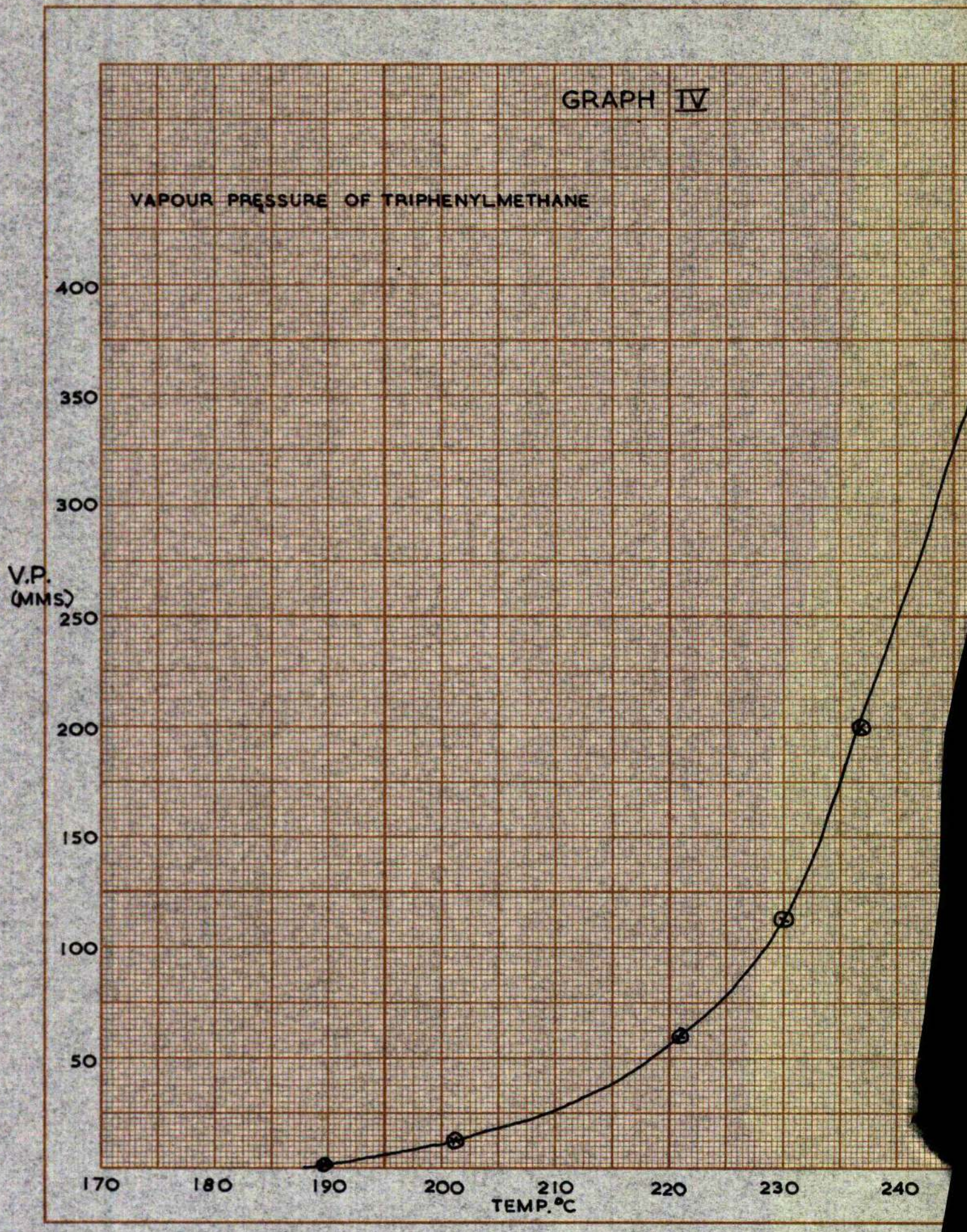
in ice and treated with 2 N ammonium chloride. Instead of the solid product expected, another oil was obtained, which, after separation was treated with a mixture of acetic and sulphuric acids. After boiling and cooling, slender white needles were obtained which were filtered off and purified by recrystallisation from methanol. They melted at 145°C, and from the spectrophotometric examination were shown to be pure 9-phenyl fluorene.

Preparation of Standard U.V. data.

The same procedure was adopted in the preparation of the standard U.V. curves for all the materials used. The method of making up the standard solution has already been described. Where published data was available in the literature, it was possible to calculate the dilutions that would be necessary over the wavelength range being used, 200 to 350 mμ.

One cell of the instrument was filled with pure solvent and the other with solution, the cells being silica of 1 cm. thickness. The slit width used was 0.2 mm. and observations were made every 2 mμ except when maxima or minima were observed, these points being traced at each 0.5 mμ.

The curves obtained for triphenylmethane and 9-phenyl fluorene are given on graph III.


GRAPH IV
VAPOUR PRESSURE OF TRIPHENYLMETHANE
V.P. (MMS)
400
350
300
250
200
150
100
50
170
180
190
200
210
220
230
240
TEMP. °C

Investigation of products of pyrolysis.

A small container was made from Pyrex glass, filled with triphenylmethane, and glass blown on to the injector system. The injector was then pumped down and the valves closed; by applying a flame carefully to the container the material was melted. The liquid bubbled violently due to dissolved air coming off. The valve was opened and shut rapidly several times when the material had cooled to one or two degress above its melting point. Liquid air was then placed round the container and the system pumped out thoroughly.

This procedure was carried out three times before the material was considered to be completely degassed.

The relation between vapour pressure and temperature for T.P.M. is shown in graph IV A v.p. of about 40-50 mms. was required to give reproducible emission from the injector and benzyl acetate boiling at 218°C was used in the container heater.

While the container was coming to thermal equilibrium the apparatus was brought to a state of readiness as described on page 39. Ice was used as a coolant on trap T.1 and liquid air on the others. The furnace, switched on earlier by a Venner time switch, was at the desired operating temperature. The mass spectrometer had been allowed to warm up until steady conditions had been

attained and the gas handling system was pumped out. Just before starting the run the gas handling system by-pass, tap T3, was closed and cut-off C.O.2 lowered. Cut-offs C.O.1 and C.O.3 were lowered, and taps T4 and T5 opened to admit the material to the circulating system. Nitrogen was then introduced from the gas measuring system to the apparatus and, when conditions were steady, the hydrogen and nitrogen voltages given by the mass spectrometer were noted. A complete scan of the background from mass 12 to mass 44, and the peaks of masses 77 and 78, was taken on the recorder.

The system was then ready for the introduction of the triphenylmethane. The mass spectrometer was focussed on H_2 (m/e = 2) and the chart started. The injector was opened and immediately the voltage of the H_2 peak began to rise. During the passage of the material the 77 and 78 peaks were examined for benzene or phenyl fragments produced. When a reasonable amount of hydrogen had been formed, the injector was closed and the container heater switched off.

Investigation of gaseous and volatile products.

The hydrogen and nitrogen peaks were noted and, by a calculation similar to that detailed on page 32, the gram moles of hydrogen produced were found. A complete scan of the masses 12 to 44 was repeated; there was no increase in any, nor was there any increase in the 77 or

78 peaks. This showed that there was no cleavage of a benzene ring from the molecule nor rupture of a ring leading to various C_1 and C_2 fractions. The absence of an increase in the mass 44 peak showed that CO_2 had not been produced; any air leak into the system would have produced CO_2 by combustion of some triphenylmethane.

The gases in the system were pumped into the gas handling system by the method detailed previously, and, after measurement of volume, were passed into the CuO furnace. After combustion of the hydrogen, the gas was returned for further measurement of volume. This provided a second estimation of the hydrogen.

Investigation of solid products.

Having evacuated the system and completed the investigation into the gaseous products, the pressure was raised to 1 atmosphere and the trap T.1 was removed. The material in the trap was a pale yellowish pink colour. Acetone, previously purified by distillation, was added to dissolve the material, and the solution was transferred to a tared beaker. The trap was thoroughly rinsed into the beaker and the solvent evaporated on the water bath. After cooling in a vacuum dessicator the beaker was reweighed and hence the amount of unreacted triphenylmethane and products was found.

This material was then dissolved in methyl alcohol and the solution made up to 100 ml. in a standard flask.

GRAPH V

U.V. ABSORPTION OF TRIPHENYLMETHANE PYROLYSIS PRODUCTS

The U.V. absorption spectrum was determined and a complete examination of a typical curve is given in graph V .

From the peaks observed at 303mμ and 292mμ in the graph, it is evident that phenyl fluorene was present. There was no absorption at wavelengths above 330mμ hence it appeared that only phenyl fluorene and triphenylmethane were present.

The method of calculating the concentration of each of the constituents is shown in the following:-

Weight of material collected in trap T.1 = 0.540 gms.

Material dissolved in methanol, volume =100 mls.

Optical density at 303mμ = .696 - (i)

" " " 292mμ = .482 - (ii)

From (i), concentration of phenyl fluorene = 0.8×10^{-4} mole/litre.

From (ii), " " " " = 0.8×10^{-4} mole/litre.

Solution diluted 50 times.

Optical density at 262 mμ = 0.393

" " " 270 mμ = 0.283

but O.D. at 262mμ due to $(0.8 \times 10^{-4})/50$ mole/litre of phenyl fluorene = 0.028

and at 270mμ = 0.025

∴ Optical density due to T.P.M. at 262mμ = 0.365 - (iii)
and at 270mμ = 0.258 - (iv)

From (iii), concentration of T.P.M. = 4×10^{-4} mole/litre.

From (iv) " " " " = 4×10^{-3} mole/litre.

Hence triphenylmethane present $\frac{4 \times 10^{-4} \times 50}{}$ x (100/1000)moles

= 20×10^{-4} moles.

Table 4.

Products from Triphenylmethane.

Run	H_2 x 10^5 gm/moles.	Phenyl Fluorene x10^5 gm/moles.	Triphenylmethane x10^4 gm/moles.
4	.80	.80	20.0
6	2.25	2.21	16.0
7	.03	.033	6.88

and phenyl fluorene present $= 0.8 \times 10^{-4} \times 100/1000$ moles.

$= 0.8 \times 10^{-5}$ moles.

Moles H_2 by mass spectrometer $= 0.79 \times 10^{-5}$

Moles H_2 by combustion analysis $= 0.80 \times 10^{-5}$

Thus the number of moles of hydrogen produced was equal to the moles of phenyl fluorene produced, and, within the accuracy of the determination, the amounts of material measured gravimetrically agreed with those obtained as a result of spectrophotometric analysis.

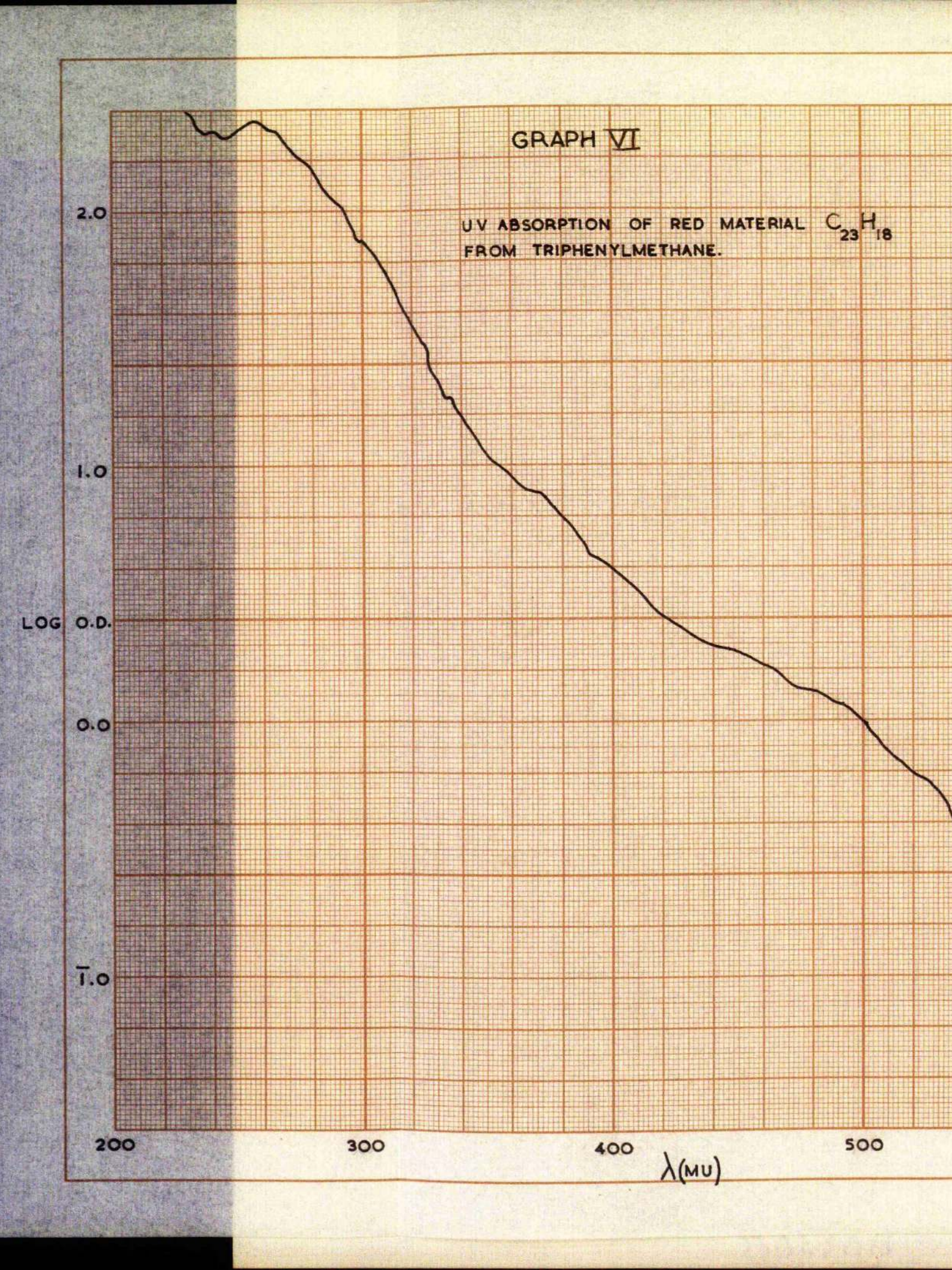
The results obtained from a further two confirmatory runs are tabulated on the page facing.

Both triphenylmethane and phenyl fluorene are colourless, but, as already noted, the colour of the material in the trap was pink. This was obviously a material present in infinitesimal amount since its existence did not prevent equivalence between the amounts of hydrogen and phenyl fluorene formed. The amount formed in a single run was quite insufficient for identification, but while the kinetic data were being obtained all the solid products were retained and treated as a whole chromatographically.

The first problem in the separation was to get rid of the enormous excess of triphenylmethane and it was found that the coloured material was rather more soluble in petroleum ether. Accordingly, the combined products were placed in a flask and petroleum ether

was added. The flask was shaken for about an hour in an electric shaker, when, after settling, the ether was decanted. The process was repeated until the ether no longer became coloured in the shaking. The combined extracts were concentrated somewhat and filtered.

A column was prepared with activated alumina, 20 cms. long and 1 cm. diameter. The petroleum solution was poured in the column and the coloured material was observed to stay at the top. The column was eluted with n-hexane and the eluate continuously examined in the U.V. spectrophotometer. The first fraction consisted of pure phenyl fluorene, followed by mixtures of phenyl fluorene and triphenylmethane and finally by pure triphenylmethane, the curve of which was identical with that obtained for the sample of the material examined in the initial preparation. This showed that the material used was, indeed, quite pure, since, had there been any impurities, they would have been separated and noticed during the chromatographic analysis. When the eluate was pure n-hexane, the eluting liquid was changed to 5% MeOH in benzene. This caused the red band to move down the column, and, as before, samples were taken, evaporated to dryness, dissolved in methanol and examined spectrophotometrically. Finally the red band was washed out, but it remained as an oil on evaporation


GRAPH VI
UV ABSORPTION OF RED MATERIAL $C_{23}H_{18}$
FROM TRIPHENYLMETHANE.
2.0
1.0
LOG O.D.
0.0
$\bar{1}.0$
200
300
400
500
λ(MU)

of the solvent. Further treatment in two more columns using pure benzene as the solvent and eluting liquid yielded finally a material which, on recrystallisation, gave clusters of orange yellow crystals. In all, 3.6 mgm. of the material was obtained from some 160 runs. A curve for the light absorption is given in graph VI.

The material melted sharply on the hot stage microscope at 68°C. A sample was sent for micro analysis* and the following report was received:-

Molecular weight 314.

Empirical formula $C_{23}H_{18}$

These figures have a numerical discrepancy of some 10% but the analysis itself was an achievement in view of the size of the sample available. Speculation on the identity of this material will be reserved for the discussion section.

Kinetic study of triphenylmethane.

In the determination of a bond strength in an organic molecule by the method outlined in the introduction, it is necessary that the rupture of this bond shall be the rate determining step of the reaction which results in the thermal decomposition of the molecule. The molecule splits up, in general, into one radical and one atom, or into two

* Micro analysis by Drs. Weiler and Strauss, Oxford.

radicals. These fragments will then undergo further reaction, either by migration of atoms or by other secondary processes and become stable entities. It is desirable to suppress these secondary reactions so that the expression for the whole reaction can be interpreted and a mechanism, capable of simple proof, be proposed.

The only products obtained from triphenylmethane have been shown to be phenyl fluorene, produced equimolecularly with hydrogen.

In order to obtain useful kinetic data on this reaction the following points have been investigated:-

(a) the effect of varying the surface area of the reaction vessel.

(b) the effect of variations in the partial pressure of triphenylmethane and in the time of reaction.

(c) the temperature coefficient of the reaction velocity.

Experimental work.

Calibration of the injector system was carried out using three different liquids in the container heater. In the calibrations the apparatus was in the same condition as in the kinetic experiments save that the furnace was below the minimum temperature for decomposition. All other components were at their normal operating temperatures. The injector was opened for 30 minutes and the material which collected in the trap at the furnace

Table 5.

Delivery of injector unit.

Liquid	B.Pt.	Moles T.P.M./ minute.	Average moles/ minute.
Benzyl Acetate.	216°C	0.760 0.758 0.752	0.756
Methyl salicylate.	222°C	1.240 1.225 1.230	1.231
Phenyl propyl alcohol.	235°C	2.470 2.300 2.320	2.366

outlet was removed, the product dissolved in acetone, and weighed after evaporation of the acetone. This was repeated three times at each bath temperature. The results are collected in table 5 .

A decomposition experiment involved opening the injector for a given length of time, noting the pressures on the McLeod gauges each minute during the run, and measuring the hydrogen produced on the mass spectrometer, checking the sensitivity of the instrument on the nitrogen peak at each reading. After a set of runs was carried out in this way the hydrogen was transferred to the gas measuring system and the total amount produced was measured by combustion. The solid material in the furnace outlet trap was dissolved in acetone and finally weighed. The product was retained. By following this system a continuous day to day check was carried out on the analysis of the hydrogen and so allowance could be made for any deviations of the injector unit from its calibrated value. These deviations were generally traced to alterations in the barometric pressure and hence to variations of the boiling point of the liquid in the container heater.

Check of first order behaviour.

As detailed previously, to establish adherence to the first order law the velocity constant had to be proved independent of surface area of the reaction vessel, time

Table: 6 Changes in Reaction Conditions.

Variation of partial pressure.

Temp. °K	Run	Time of contact secs.	Partial pressure mm.Hg.	k (sec^{-1})
963	18	,482	.68	.0101
	101	.439	.18	.0088
1006	76	.423	.346	.0338
	162	.397	.136	.0394
984	22	.418	.075	.0318
	29	.427	.152	.0308

Variation of Time of Contact.

Temp. °K	Run	Time of contact secs.	Partial pressure mm.Hg.	k (sec^{-1})
996	12	.342	.124	.0310
	113	.702	.182	.0295
1003	125	.76	.193	.0388
	160	.212	.182	.0400
1003	118	.498	.182	.0400
	119	.865	.216	.0389

Variation of Surface Area.

Temp. °K	Run	Time of contact secs.	Partial pressure mm.Hg.	k (sec^{-1})
1049	46	.386	.118	.2065
	166p	.519	.183	.2098
1055	150	.450	.160	.2335
	169p	.517	.184	.2349
1056	50	.262	.081	.2270
	171p	.501	.179	.2294

---

of contact, and partial pressure.

Partial pressure.

The partial pressure of the reactant was varied by altering the temperature of the container heater, thus varying the amount of material injected into a given pressure of nitrogen.

The results of the runs are given in table 6 .

Time of contact.

The speed of pumping the circulating nitrogen could be altered by changing the temperature of the heater bath of the circulating pump. The time of contact is the time of residence of a molecule in the reaction vessel and is derived as follows:-

Using the relationship PV/T constant, the volume of a mole of gas under the conditions obtaining in the reaction vessel may be expressed as

$V = \frac{P_1}{P} \cdot \frac{T}{T_1} \cdot V_1$ where P_1, V_1, T_1 refer to normal temperature and pressure.

$$\text{The time of contact, } t = \frac{\text{volume of furnace.}}{\text{volume of gas/second.}}$$

$$= \frac{\text{volume of furnace} \times T_1 \times P}{P_1 V_1 T \times \text{rate of flow of gas in moles/second.}}$$

In flow systems of the type used in this work it is experimentally difficult to alter the time of contact without producing a change in the pressure within the reaction vessel, both of the carrier gas and the reactant.

Careful manipulation of the total quantity of gas in the system enabled the pressure of the carrier gas to be maintained constant for different flow rates, while in order to adjust the reactant partial pressure, the number of moles injected had to be varied.

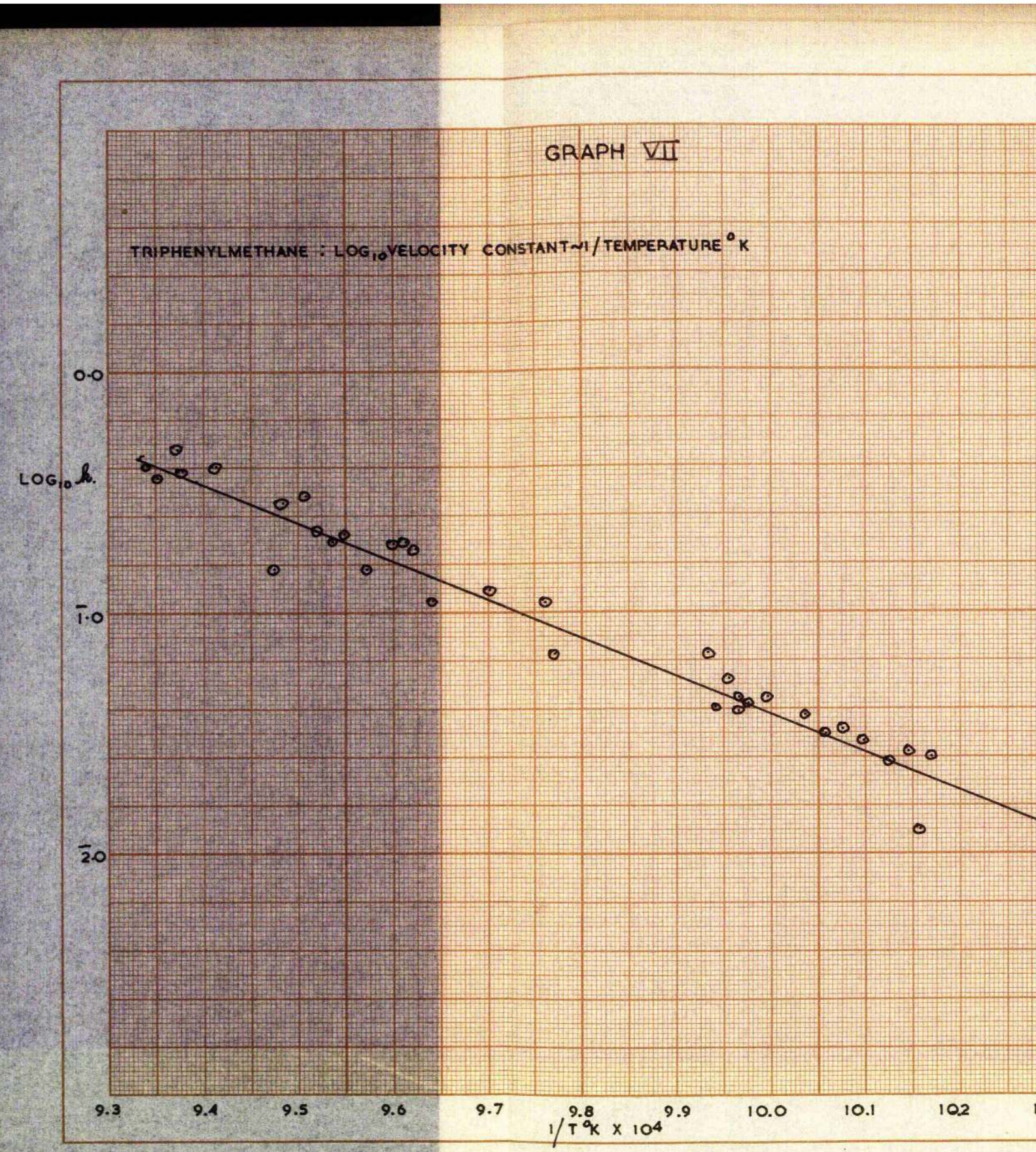
Table 6. shows the results of the series of experiments.

Surface area of reaction vessel.

The surface area of the furnace was altered by placing silica wool in the furnace. The wool used had a surface area of 1136 sq.cm. per gram and the 3.17 gms. taken represented an area of 3601 sq.cms. The effective surface area of the furnace was 514 sq.cms., hence the introduction of the wool represented an eight-fold increase in area.

Runs done in the packed furnace are compared with those done in an unpacked furnace, in table 6.

The data given in the three tables show that triphenylmethane undergoes thermal decomposition by a unimolecular mechanism and further experiments were carried out to estimate the velocity constant of the decomposition over a range of temperatures. The range selected covers 132° from 939° to 1071°K and full details are tabulated in the section dealing with the experimental results. The logarithm of the weighted mean of the velocity constants at each temperature is plotted against the reciprocal of


GRAPH VII
TRIPHENYLMETHANE : LOG10 VELOCITY CONSTANT ~ 1/TEMPERATURE °K
LOG10 k.
0·0
1̄·0
2̄·0
9.3
9.4
9.5
9.6
9.7
9.8
9.9
10.0
10.1
10.2
1/T °K X 10⁴

of temperature on graphVII giving a linear relationship from which the activation energy may be deduced.

Calculation of the results of a run.

(a) Treatment of mass spectrometric data.

In all mass spectrometric analyses a current of ions produces a voltage V across the grid resistor of the amplifier and this is the output quantity supplied by the instrument. The input to the instrument consists of a rate of flow of a gas through a leak system and is produced by a pressure p mm. of the gas in the sample system. It is the constant aim in the use of the mass spectrometer for analysis to keep the sensitivity factor (p/V) constant by standardisation of conditions.

In the present work the volume occupied by the sample was the kinetic flow system and by direct measurement of gas pressures it is possible to calibrate the instrument and derive relationships of the type $p_{H_2} = \alpha V_{H_2}$ and $p_{N_2} = \beta p_{N_2}$. The values of α and β tended to change from day to day but the ratio α/β was constant. (The change referred to probably results from ion source conditions being disturbed by the instrument being used for a variety of purposes.)

It is very desirable in mass spectrometry to perform the necessary calibrations soon after the measurement of an unknown concentration and this was difficult to achieve for hydrogen during a kinetic run. An internal

standard for calibration was available, however, in the nitrogen of the circulating system. Observations were therefore recorded of $p^1_{N_2}$, $V^1_{N_2}$, $V^1_{H_2}$ - the pressure of nitrogen and the output voltages for nitrogen and hydrogen taken at intervals during a run. The unknown and desired pressure of hydrogen can be obtained by use of the relationships -

$$\frac{p^1_{H_2}}{V^1_{H_2}} \Big/ \frac{p^1_{N_2}}{V^1_{N_2}} = \alpha \Big/ \beta = \frac{p_{H_2}}{V_{H_2}} \Big/ \frac{p_{N_2}}{V_{N_2}}$$

$$p^1_{H_2} = \alpha/\beta \cdot V^1_{H_2} \cdot (p^1_{N_2} / V^1_{N_2}) \cdot$$

In practice it was more convenient to derive $n^1_{H_2}$ = number of moles H_2 in the circulating system corresponding to $p^1_{H_2}$mm. Clearly $n^1_{H_2} = \gamma\, p_{H_2}$ where γ is a constant determined by the volume and temperature of the apparatus.

This leads to

$$n^1_{H_2} = \gamma . \alpha/\beta \; V^1_{H_2} \cdot (p^1_{N_2} / V^1_{N_2}) \quad .$$

Similarly the injection of a known number of moles of hydrogen (n_{H_2}) from a gas burette during initial calibration establishes

$$n_{H_2} = \gamma\, \alpha/\beta \; V_{H_2} \cdot (p_{N_2} / V_{N_2})$$

From these last equations the constants can be eliminated:-

$$n^{1}_{H_2} = n_{H_2} \cdot \frac{V_{N_2}}{p_{N_2}} \cdot \frac{1}{V_{H_2}} \cdot V^{1}_{H_2} \cdot \frac{p^{1}_{N_2}}{V^{1}_{N_2}}$$

In practice during calibrations with hydrogen and nitrogen a plot of n_{H_2} against $V_{H_2}\left(\frac{p_{N_2}}{V_{N_2}}\right)$ was made and the slope taken in order to use this expression.

(b) Application to a particular example.

Furnace temperature = 723°C.

Duration of run = 7 mins. 23 secs.

T.P.M. injected into apparatus = 6.48×10^{-4} moles.

Initial pressure at leak of mass spectrometer = 4.60mm.

Initial voltage of nitrogen = 4.34v.

Initial voltage of hydrogen = 210mv.

Sensitivity of mass spectrometer = 4.60/4.34 mm/v for N_2.

$\therefore$ β x (voltage of hydrogen) = 210mv x 4.60mm/v/4.34=222mm.

Mc Leod gauge pressures:

4.67, 3.10; 4.70, 3.05; 4.67, 3.05; 4.65, 3.15;

4.65, 3.05; 4.65, 3.10.

Final pressure at leak of mass spectrometer = 4.67mm.

Final voltage of nitrogen = 4.304v.

Final voltage of hydrogen =264.9mv.

Sensitivity of mass spectrometer = 4.67/4.30.

$\therefore$ β x voltage of hydrogen = 264.9x4.67/4.30 = 287mv.

$\therefore \Delta$. (β x voltage of hydrogen) = 65mv.

From calibration of instrument, moles H_2 produced = $.07 \times 10^{-4}$

Rate of flow of gas in system = capillary constant x $\left(\frac{\text{higher McLeod pressure}}{\text{lower McLeod pressure}}\right)^2$

$= 5.310 \times 10^{-6} \times 12.19.$

Time of contact = 0.342 seconds.

Hence $k = \frac{2.303}{0.342} \log. \frac{6.48 \times 10^{-4}}{(6.48 - .07) \times 10^{-4}} = 0.0310 \text{ sec}^{-1}.$

Use of deuterium as carrier gas.

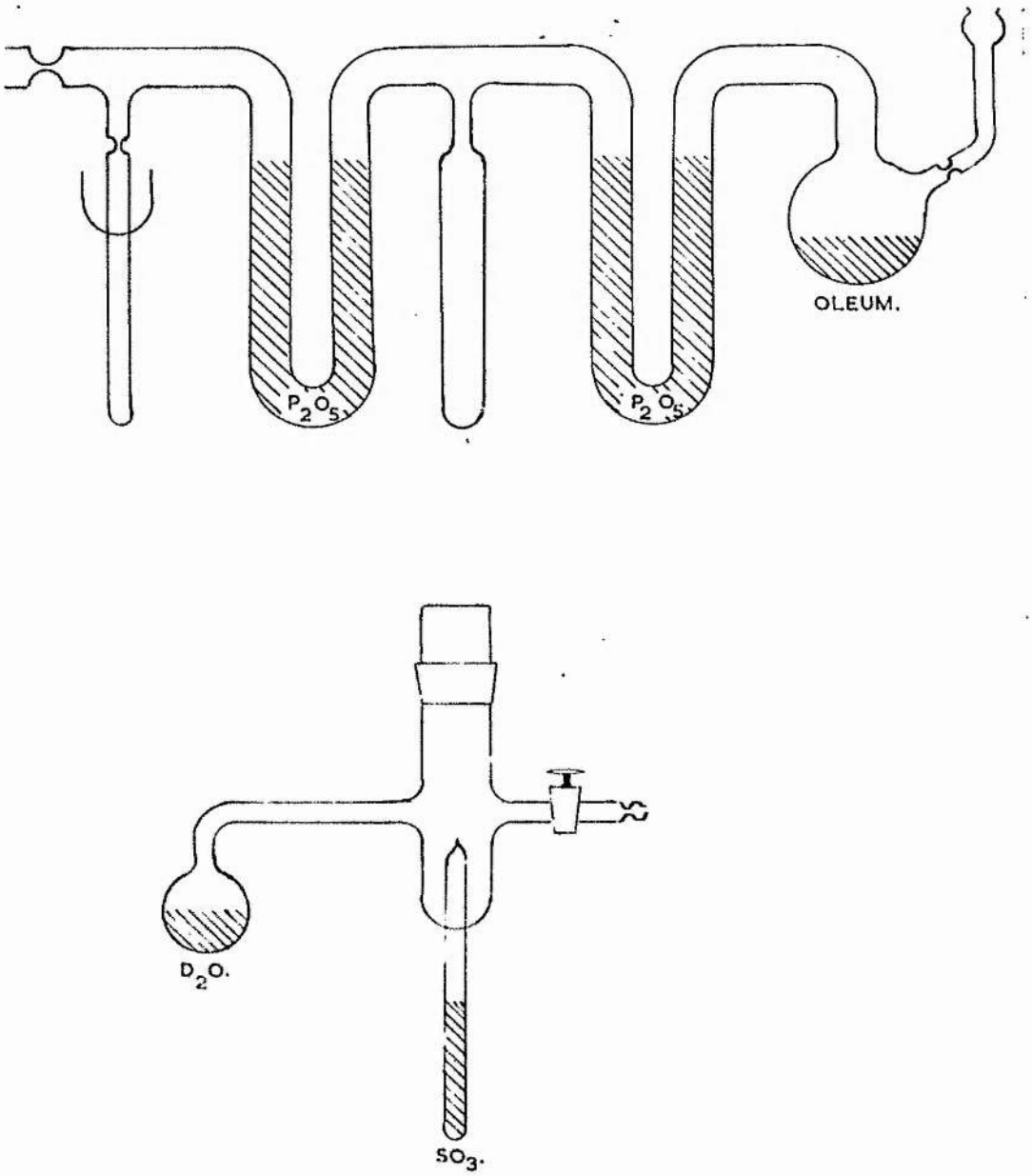
The decomposition of triphenylmethane to yield phenyl fluorene and hydrogen was thought to proceed by loss of the methylenic hydrogen atom giving, as an intermediate product, the triphenylmethyl radical. In an endeavour to prove the existence of hydrogen atoms in the system, deuterium was used as the carrier gas in the circulating system. With this considerable concentration of molecules of D_2 a reaction with hydrogen atoms would be expected according to the following equation:-

$$H + D_2 \longrightarrow HD + D$$

Thus, when carrying out this experiment, the D_2 peak on the mass spectrometer (mass 4) should fall as the HD peak (mass 3) rises. If phenyl fluorene was made from triphenylmethane by elimination of a complete molecule of hydrogen in one stage then the formation of HD should be slight.

DIAGRAM 8.

APPARATUS FOR THE PREPARATION OF D_2SO_4.



Preparation of deuterium.

The preparation of sulphur trioxide was carried out using oleum as starting material. The apparatus shown in diagram 8 was made. It consisted of a container for the oleum and a train of phosphorous pentoxide traps, each pair being separated by a containing vessel of about 10mls. capacity into which the SO_3 could be frozen by a suitable cooling bath. Trouble was experienced through the P_2O_5 traps blocking up but this was overcome by filling the traps with long glass wool fibres as a base for the P_2O_5 powder. When the SO_3 had been collected in the first container, the oleum boiler was detached, the system sealed at one end, and attached to a high vacuum system at the other. When the pressure was lowered to 10^{-5}cms. mercury, the pumping end of the system was sealed and the SO_3 was distilled to and fro through one of the P_2O_5 traps. This repeated distillation was continued until the SO_3 melted at 16°C. A calculated volume was finally collected in the third container which was removed and sealed. The container was then attached to the apparatus shown in the lower diagram, containing pure deuterium oxide in the flask. With a solid carbon dioxide cooling bath round the D_2O the system was evacuated and sealed off. The cooling baths round the D_2O and the SO_3 were very gradually lowered to allow the SO_3 to distil over to the D_2O. Thus D_2SO_4 was prepared of definite concentration, (6N), to give a suitable electrical conductivity for the next step of

the preparation.

Deuterium gas was obtained by electrolysis of the deutero-sulphuric acid, the system being evacuated before starting the electrolysis. The gas was stored in 2 litre flasks and, before using it, a check for the content of hydrogen was made by means of the mass spectrometer.

Mass Spectrometry of H_2 and D_2.

Hydrogen and deuterium can be brought into equilibrium with hydrogen deuteride according to the equation:-

$$H_2 + D_2 \rightleftharpoons 2HD$$

an equilibrium constant, $K = p_{HD}^2 / p_{H_2} \cdot p_{D_2}$, being known at different temperatures. The equilibrium can be brought about by thermal reactions of H_2 and D_2 (by a route involving atoms) or by catalysts.

For very accurate analytical work by mass spectrometry on mixtures containing the species D_2, H_2 and HD it is essential to take several precautions during calibrations and estimations. These precautions are discussed in detail by Kirshenbaum.[57] The ions produced from such mixtures can be:-

Mass	1	2	3	4	5	6
Ions	H	H_2D	H_3HD	D_2 H_2D	HD_2	D_3

The ions H_3, H_2D, HD_2, D_3, are formed by collision of a positive ion with a molecule and as a result, the amounts formed are dependent on the square of the pressure.

Table 7.

Temp. ^{o}A.	Press. D_2	Moles T.P.M.	p.p. T.P.M. (mms)	Time of run mins.	Peak Voltages.		
					4	3	2
1061	3.5 mm.	2.5×10^{-3}	0.563	0	15	0.54	0.235
				9	5.85	5.77	3.50
1078	3.62mm.	1.01×10^{-3}	0.409	0	18.75	0.6	0.415
				5	10.56	6.0	2.10

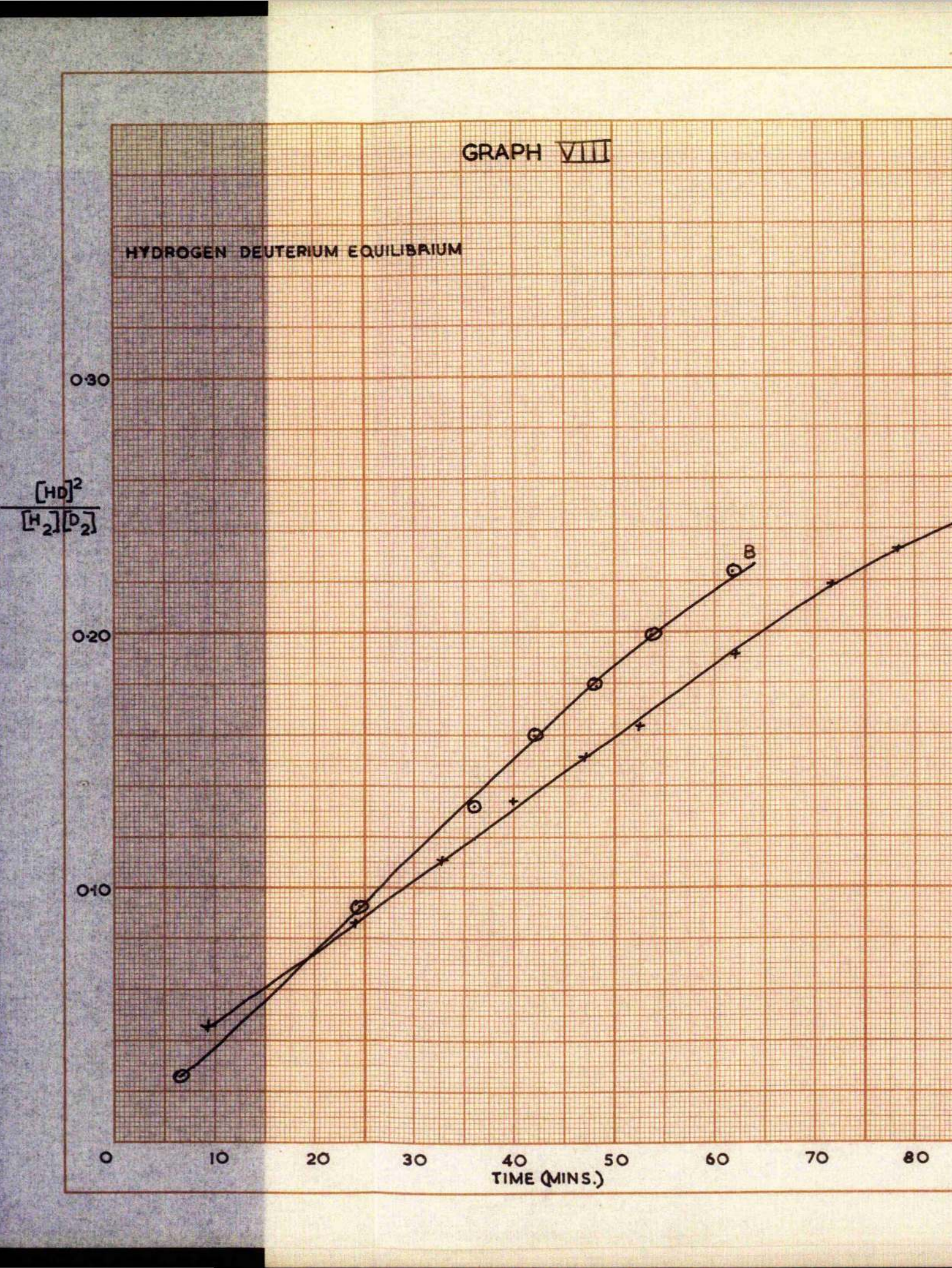
At the lower operating pressures in the mass spectrometer used, such bimolecular processes are unlikely events and, since the work with deuterium reported here is essentially a survey of a rough quantitative character, it was not considered necessary to correct for the small errors introduced for masses 3 and 4. If correction had been required it would have been necessary to study the pressure dependence on the ion currents for these masses and eliminate the conditions made by the bimolecular collisions of ions and molecules.

Experimental work with Deuterium.

The first run was carried out at 788°C and the second run at 805°C. The procedure was identical with that previously employed except that a record was kept of the decrease in the mass 4 peak (D_2), and the increases in the mass 2 and mass 3 peaks, H_2 and HD respectively.

The results of the two runs are given in table 7 showing that at 788°C, 3.27 volts hydrogen were formed compared with 3.50 calculated from the previous runs with nitrogen carrier gas. In the second run the H_2 figures were 1.68 and 1.77.

From the results, the decrease in D_2, and the corresponding increase in the HD peak, were quite beyond what had been expected. It was considered that an experiment should be performed to test the rate of


GRAPH VIII
HYDROGEN DEUTERIUM EQUILIBRIUM
$\frac{[HD]^2}{[H_2][D_2]}$
0·30
0·20
0·10
0
10
20
30
40
50
60
70
80
TIME (MINS.)
B

HD formation from mixtures of H_2 and D_2 at the temperature of the pyrolysis.

Deuterium was circulated through the apparatus with the furnace at 800°C; its voltage was noted on the mass spectrometer. A definite amount of hydrogen was then introduced to the circulating system from the gas burette shown in diagram 5. Observations were made of the pressures on either side of the flow capillary in the apparatus by means of the twin McLeod gauges and also of the voltages of masses 2, 3, and 4 on the mass spectrometer. Assuming the sensitivities of the three gases to be equal, $\frac{(V_{HD})^2}{(V_{H_2})\ (V_{D_2})}$ was calculated for each set of observations and these values were plotted against time.

The results of two such experiments are shown in graph VIII. In graph A, 2.63×10^{-5} moles hydrogen were injected and in graph B, 3.6×10^{-5} moles.

These graphs show that even after 1½ hours continuous circulation the amounts of HD produced by reaction of H_2 and D_2 would not be a significant contribution to the amount produced when triphenylmethane was pyrolysed in deuterium. Moreover, the value of the equilibrium constant expression given above was far below the known value of 3.8 at 500°C for $H_2 + D_2 \longrightarrow 2HD$.[58] This suggests that the significant method of production of HD in the runs carried out with triphenylmethane must be a route involving

free atoms of hydrogen.

In the first run with triphenylmethane, using deuterium as carrier gas, deuterium equivalent to a reading of 9.15 volts was "lost" during the reaction. A reading of 5.23 volts of HD accounts for 2.6 volts of D_2, leaving 6.5 volts to be accounted for. This deuterium could only have gone into the solid product and hence carbon and hydrogen analyses of this material were carried out.

A modified form of the apparatus advocated by Pregl[59] was employed. Oxygen gas from a cylinder was bubbled through a sulphuric acid trap before being passed through a silica tube three feet long, two-thirds packed with specially pure copper oxide, a commercial grade manufactured by oxidation of pure copper wire. From the furnace the gas passed through a glass spiral immersed in liquid air, then through a sulphuric acid trap to the atmosphere. The possibility of atmospheric moisture condensing in the spiral was eliminated.

A known weight of material was burned in the tube and the CO_2 and water condensed in the spiral, which was then removed and evacuated over liquid air. Once evacuated, the freezing bath was changed to CO_2 and acetone and the CO_2 produced in the combustion was allowed to distil into a trap cooled in liquid air. The contents of this trap

Table: 8. Analysis of deuterated phenyl fluorene.

Carbon Dioxide.

Volume of apparatus = 10 litres.

Pressure increase = 20mm.

Moles gas = 10.95×10^{-3}

Moles gas from 0.1547 gms. sample. = 12.0×10^{-3}

Water.

Pressure in handling system = 0.24mm.

∴ Moles in handling system = 1.31×10^{-4}

Mass	Background voltage mV	Sample voltage mV
15	37	37
16	76	98.3
17	195	570
18	695	1980
19	24.5	47.7
20	19.5	32.7

1.31×10^{-4} moles water gives an increase in voltage of 1321mv.

∴ Moles DOH $\frac{23.2}{1320} \times 1.31 \times 10^{-4} = .232 \times 10^{-5}$

Moles D_2O $\frac{13.2}{1320} \times 1.31 \times 10^{-4} = .131 \times 10^{-5}$

Theoretical quantity of water from sample = 51×10^{-4} moles.

Hence moles D_2 as DOH = 17.8×10^{-5}

and moles D_2 as D_2O = 20.1×10^{-5}

∴ Total moles = 37.9×10^{-5} ≡ 6.20 volts.

were expanded at room temperature into a previously evacuated known volume, and, from pressure measurement, the amount of CO_2 produced was estimated.

A fraction of the water remaining in the -80° trap was next expanded into the handling system of the mass spectrometer and the increases in voltages for ion masses 18, 19 and 20 noted. By calibrating the instrument with water, these voltage increases were convertible into moles. The results are given in the table opposite.

It is seen that the voltage of deuterium, 6.20 volts, is within experimental error with the 6.5 volts "lost" during the run.

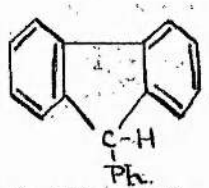
D I S C U S S I O N.

The experimental work described in previous sections shows that triphenylmethane undergoes thermal decomposition in a homogeneous gas phase reaction which follows a first order law. The rate constant for this process is given by the equation:-

$$\log_{10} k(sec^{-1}) = 14.1 - (71,100/4.57T).$$

During the progress of this work it was necessary to have a working hypothesis to guide experiments and, as has been indicated, it was considered that the essential steps in the reaction could be formulated as follows:-

$$Ph_3C - H \xrightarrow[(1.)]{} Ph_3C - + -H \xrightarrow[(2)]{}$$



$$+ H_2. \quad (a)$$

It has been shown that the essential products of the decomposition consist of equimolecular proportions of phenyl fluorene and hydrogen.

In addition, a minute amount of an orange yellow material of empirical formula (by micro-analysis) $C_{23}H_{18}$, molecular weight 314 and melting point 68°C, was observed. An exhaustive survey of the literature did not suggest a likely substance with as high a molecular weight and yet of such a low melting point. It is of interest to note, however, that when determining the latent heat of sublimation of hexaphenylethane, Cuthbertson and Bent[60] found that the material dissociated and also produced

an unidentified yellow substance of high molecular weight. This substance is not regarded as being of significance for the main features of the reaction.

It is also possible to view the reaction as occurring in one stage:-

$Ph_3C - H \longrightarrow$ 9-phenyl fluorene $+ H_2$ (b)

and to assume that the hydrogen is eliminated as a complete molecule in one stage when forming the cross link between the nuclei.

It is reasonable to summarise the evidence in favour of route (a) first.

A study of the pyrolysis of diphenylmethane[2] showed that fluorene, tetra phenyl ethane and hydrogen were formed. When 1,1 - 2,2 tetra phenylethane[2] was pyrolysed, fluorene and hydrogen were also formed. This research suggested that fluorene was formed readily from the diphenylmethyl radical in the thermal decomposition mentioned. There is no reason to doubt that in 1,1 - 2,2 tetra phenylethane the central C - C bond is the weakest link and that Ph_2CH - radicals will be formed on heating. The occurrence of these radicals in the pyrolysis of diphenylmethane involved the breaking of the stronger C - H link but the presence of the diphenylmethyl radicals at the reaction temperature is evident from the isolation of 1,1 - 2,2 tetra phenylethane in addition to fluorene. The kinetic analysis of the data gave a consistent picture for

diphenylmethane when a mechanism analogous to (a) was assumed.

In the case of triphenylmethane the pyrolytic evidence described previously did not include the isolation of any hexa phenylethane. Presumably the triphenylmethyl radical is not as stable thermally with respect to fluorene formation. This is unfortunate from the point of view of providing evidence to support route (a) but the absence of hexaphenyl ethane from the products does not eliminate this mechanism. It is known that all the compounds $Ph_3C\text{-}X$ ($X = Cl, Br, I, NH_2$) give equimolecular amounts of phenyl fluorene and HX on pyrolysis.[43] The C-X bonds of these compounds must all be weaker than the similar C - H bond in the parent hydrocarbon and so readily disrupted thermally. This evidence would suggest that the thermal conversion of the triphenylmethyl radical to the phenyl fluorene structure is an easy process. The involatility of hexaphenylethane prevented a direct test of its pyrolytic decomposition with the available apparatus and in order to get separate evidence for stage (1) of process (a), the experiments with deuterium as a carrier gas have to be considered. The results given earlier showed quite certainly that free atoms and radicals must be present in decomposing triphenylmethane in order to cause the extensive production of HD molecules which was observed.

If we conclude from this evidence that process (a) (1) is probable, then the details of stage (a) (2) can

be considered. The hydrogen atom and radical formed by (a) (1) were produced in presence of deuterium (3.5mm) and triphenylmethane (0.56mm), and the following reactions of the hydrogen atom seem relevant

Isotopic exchange.

$$H\text{-} + D_2 \longrightarrow HD + D\text{-} \qquad (a)\ (3)$$

$$D\text{-} + H_2 \longrightarrow HD + H\text{-} \qquad (a)\ (4)$$

$$D\text{-} + Ph_3C\text{-}H \longrightarrow Ph_3C\text{-}D + H\text{-} \qquad (a)\ (5)$$

Hydrogen abstraction.

$$H\text{-} + Ph_3C\text{-}H \longrightarrow Ph_3C\text{-} + H_2 \qquad (a)\ (6)$$

$$D\text{-} + Ph_3C\text{-}H \longrightarrow Ph_3C\text{-} + HD \qquad (a)\ (7)$$

Certain analogous reactions for the CPh_3- radical can be written down but the only significant one would be the attack on deuterium to produce CPh_3D. This is endothermic to the extent of some 30 K.cals. and cannot be of any importance; accordingly, such reactions of the triphenylmethyl radical are ignored.

It is known that reactions (3) and (4) have activation energies of the order of 5K.cals.[61,62] but there is no direct evidence for the processes (5, 6 and 7). It is quite certain, however, that (6) and (7) are exothermic to the extent of about 30 K.cals. A considerable amount of evidence exists on the abstraction of hydrogen atoms by methyl radicals at moderate temperatures,[63,64] and it is known that activation energies for these processes decrease from

about 10 K.cal. for breaking of a primary C - H link to 7 K.cal. for a tertiary C - H link. The bond strengths for C - H decline from 97 to 90 K.cal.[64,65,66] in the same order. There is an expected relationship, due to Polanyi, of the form $\Delta E = \alpha \Delta(\Delta H)$, where ΔE is the change in activation energy, $\Delta(\Delta H)$ the change in heat of reaction and α a constant of magnitude about 0.5, for a series of reactions of a given type. From this, we might anticipate that for the reaction $CH_3 - + Ph_3C - H \rightarrow CH_4 + CPh_3 -$, where the bond to be broken is admittedly of the order 70 - 75 K.cals., the energy of activation might well be as low as 1 to 3 K.cals. For similar reactions involving hydrogen and deuterium atoms, the evidence of Darwent and Roberts[67] suggests that a parallel lowering of activation energy occurs as the C - H bond is weakened. They have also shown that the activation energy for the $(D- + R-H)$ reaction is some 1.3 K.cal. less than for $(CH_3- + R-H)$ with a given hydrocarbon R - H. Thus, it might be a reasonable anticipation that the activation energy for reactions (6) and (7) is very low - possibly 0 - 2 K.cals.

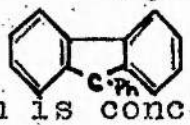
Such considerations are particularly useful when we attempt to deal with the data from the experiments with deuterium. We have used the fact of HD production as an indication of a free radical mechanism, but, in addition to this information, the experimental data showed that the H_2 production was almost the same as in work with nitrogen

as a carrier gas.

As pointed out earlier the expression $(V_{HD})^2/(V_{D_2})\cdot(V_{H_2})$ measures the equilibrium constant for the $H_2 + D_2 \rightleftharpoons 2HD$ equilibrium and the values in Table 7 for the mixtures at the end of the runs produce values of 1.48 and 1.62 for this expression. The true equilibrium position corresponds to a value of 3.8 and this demonstrates that the production of H_2 has exceeded the rate of isotopic exchange.

Molecular hydrogen can be formed by the following routes:-

$H- + Ph_3C - H \rightarrow Ph_3C- + H_2$ (a)(6)

$Ph_3C - \longrightarrow$  $+ H_2$ (a)(8)

The latter reaction is conceivably a stage in the production of phenyl-fluorene, further comments on which are given below.

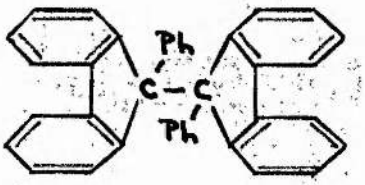
Since reaction (a)(6) is likely to have a low energy of activation, hydrogen atoms formed in the primary step might be captured by Ph_3CH as well as by D_2. The activation energy for reaction with D_2 at 5K.cals. is, indeed, probably the higher of the two alternatives, but the absence of data on the temperature independent factors in the equations of type $k = Ae^{-E/RT}$ prevents any firm decision on the preferred process. Considerable argument exists on values of temperature independent factors for radical and atom reactions and there seems to be more uncertainty about this factor than about energies of activation. A definite decision, therefore, cannot be reached by means of these argument applied to deuterium work as to whether (6) or (8) produces the molecular H_2. But the simpler assumption to explain the facts is that reaction (a)(6) is a more rapid process than the

isotopic exchanges (3) and (4).

The considerable deuteration of triphenylmethane should be noted. The process involved is presumably (a)(5), although replacement of nuclear hydrogen atoms is possible. The gram atoms of deuterium in the organic compounds emerging from the furnace represent 0.6 atoms per molecule. The readiness of this exchange process may arise from the same factors which make the hydrogen abstraction reaction an easy process.

The transformation of triphenylmethyl radical to a fluorene molecule is a process about which there is little evidence.

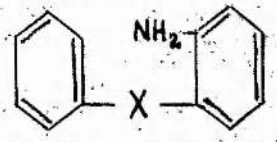
It has been known for a long time that yellow solutions of triphenylmethyl when placed in sunlight yield diphenyl-bis-diphenylene ethane[68]:-



It has been shown also that the most effective wave lengths are those absorbed by the triphenylmethyl radical, and that it must be a reaction of the latter and not of hexaphenylethane[69,70,71]. The evidence from thermal reactions has been mentioned above, and would support, if it does not prove, this point. Waters[72] has suggested that the process is of the nature of a disproportionation reaction:

$$2\ Ph_3C\text{-} \longrightarrow \text{Fluorene} + Ph_3C\text{-}H \qquad (a)(9)$$

It is possible that this can occur in one stage on suitable collisions; it is certainly true that if it

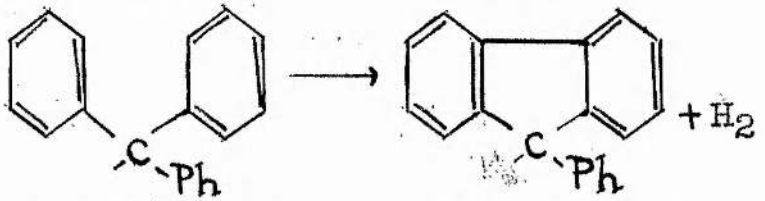
proceeds in two stages and a hydrogen atom can be removed from the ortho position of one of the rings, so producing a free valancy, then the formation of a 5-membered ring can follow. D.H. Hey[73] has shown recently that inter-nuclear cyclisation can occur to some extent during the decomposition of diazotised 2-amino-diphenylmethane, and yields fluorene. By comparison of different compounds of the  type, he suggested that the distance apart of the two ortho positions influenced the yield of the cyclisation. If this factor was important, the approximate planarity of the triphenylmethyl radical would be of great assistance when compared with the tetra-hedral arrangement in the hydrocarbons.

Little is known of the reactivity of different positions in free radicals although theoreticians have recently shown interest in this problem. In so far as homolytic reactivity is concerned, the quantity "free valance" as calculated for various positions of a molecule or radical is considered to give an indication of the relative reactivity of these positions. Mde. Alberte Pullman[74] in a discussion of the aromatic free radicals, points out that there should be a higher concentration of free valence in the ortho positions than in the para positions for the triphenylmethyl radical. Such calculations are very inexact, however, although the broad conclusions from them seem in order, and in agreement

with the thermal behaviour of triphenylmethyl radicals.

In summarising the possibilities for the conversion of triphenylmethyl radicals to fluorene we can observe the following points:-

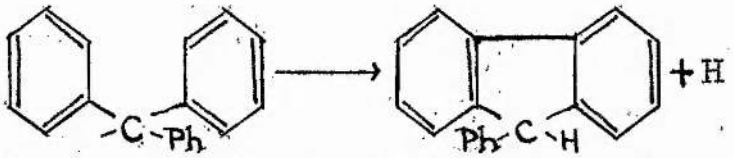
(1) A process of the type -



(a) (8)

provides H_2 molecules but leaves a radical which would be expected to dimerise. No such dimer was found.

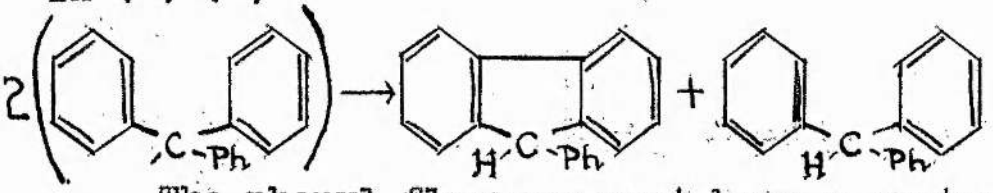
(2) The reaction -



(a) (10)

would provide phenyl fluorene as found but the free atom by reaction with parent hydrocarbon could reform the radical on the left hand side and so start a chain.

(3) The only solution to the difficulties of (1) and (2) appears to be a disproportionation process as in (a) (9) -



(a) (9)

The phenyl fluorene must have a central C - H link of about the same strength as that in triphenylmethane and some decomposition of it would be expected. But with the small percentages of decomposition of triphenylmethane

which have been employed in the present work, the amount of products to be expected would be negligible.

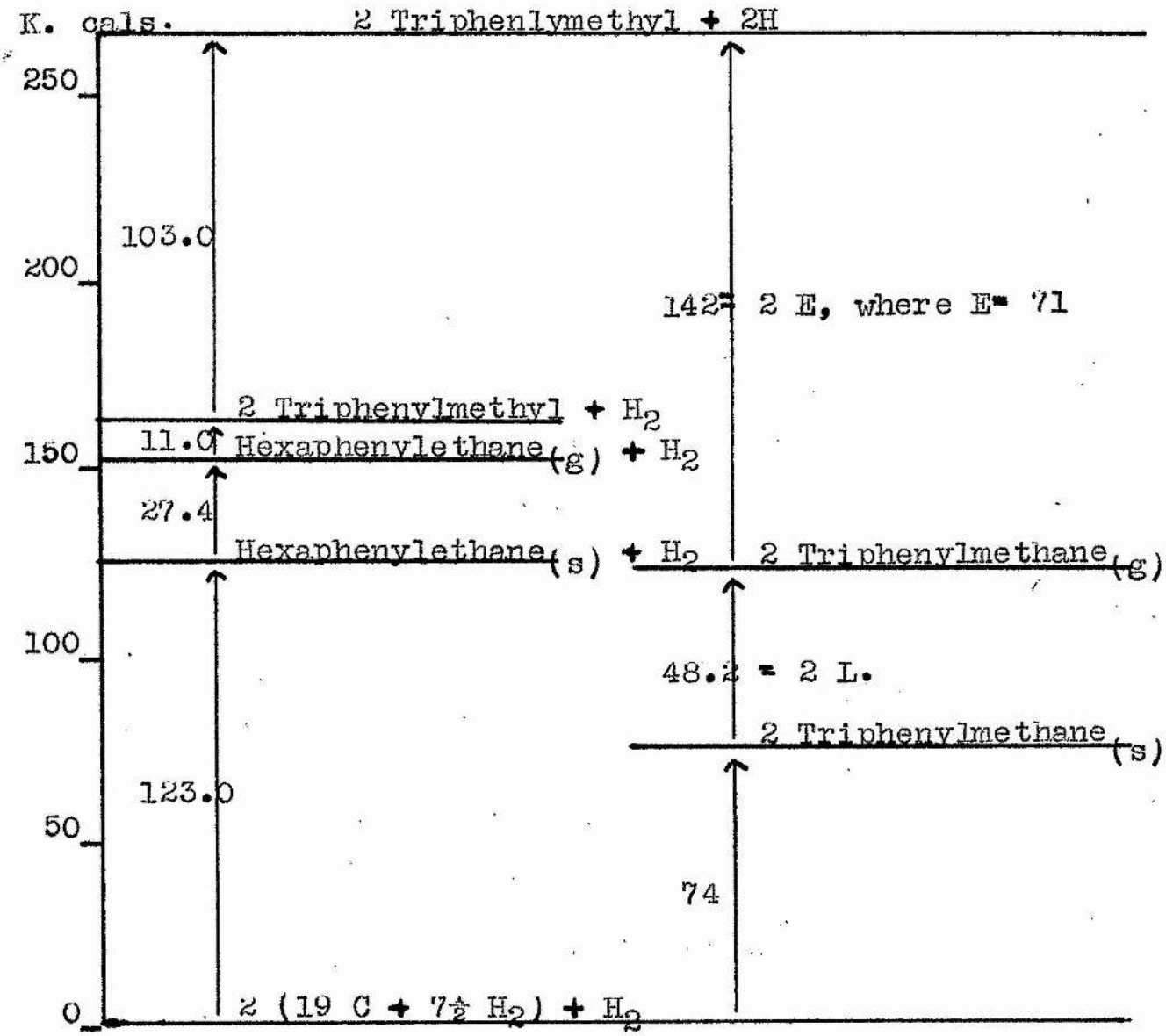
The conclusions from this survey are that the rate determining step of the reaction is the dissociation $Ph_3C\text{-}H \longrightarrow Ph_3C\text{-} + \text{-}H$, which has an activation energy of 71 K.cals; this corresponds to the bond strength of the link broken. This reaction is followed by $H + Ph_3C\text{-}H \longrightarrow Ph_3C\text{-} + H_2$ and the production of phenyl fluorene from the triphenylmethyl radical probably involves disproportionation process.

From the above conclusions we can suggest that the energy of activation of 71 K.cals. is the bond dissociation energy of the C - H bond in Ph_3C - H. It is to be expected that this bond energy will be low in view of the large resonance energy of the triphenylmethyl radical. The current ideas of the stability of this radical are largely based on the classical work on the heat of dissociation of hexaphenyl ethanes which features in many text books and will not be detailed. An independent estimate of the resonance energy of the radical is valuable, however, as the hexa-aryl ethane work was all done in solutions. Moreover, the precise part played by steric effects in the aryl ethanes has been a matter of dispute. The present work suggests that the C - H bond in Ph_3CH is 30 K.cal. weaker than the similar bond in methane.

In relating these data to other thermochemical

Table 9.

Thermochemical Data.



quantities, the following data have been used.

Heat of combustion of hexaphenylethane:

A value has been obtained by extrapolation from the data of Coops et al[75] on the heats of combustion of the solid phenylated ethanes.

PhEt	1089.94 K.cals.
$Ph.CH_2CH_2.Ph$	1805.7
$Ph_2.CH.CH_2.Ph$	2526.0
$Ph_2.CH.CH.Ph_2$	3248.2
$Ph_3.C.CH.Ph_2$	3987.4

Taking the increment per phenyl group to be 739.2 K.cals. in the relevant region, this enables an estimate of 4726 K.cals./mole to be made for the heat of combustion of hexaphenylethane.

Using 94.05 and 68.3 K.cals./mole for the heats of combustion of carbon and hydrogen respectively, we get the equation:-

$$38C_s + 15H_{2(g)} \longrightarrow C_{38}H_{30} - 123 \text{ K.cals.}$$

Latent heats of sublimation:

Triphenylmethane	24.1 $\pm$ 1.K.cal.
Hexa-phenyl ethane	27.4 $\pm$ 1.5 K.cal.

Heat of combustion of triphenylmethane = 2373.

The results of this analysis can be seen most readily by reference to the table opposite, where a consistent scheme emerges. The only data with which these values

can be compared are figures due to Bent[76] on the heat of hydrogenation of hexaphenylethane to two molecules of triphenylmethane. He concluded that this reaction was exothermic to 40.5 K.cal. with the materials as solids and 34.8 K.cals. for solutions of the compounds.

The energy level difference derived from combustion data is 49 K.cals. (123 - 74) for the solids or 28 K.cals. in the vapour phase. The agreement here is only of a rough order but the uncertainties of unknown heats of solutions may explain it.

CARBAZOLE.

Pyrolysis of Carbazole.

Carbazole has interested the chemist for almost a century, and papers relating to the work to be described date from a time when the pure material could not have been isolated from its natural sources. Purification of crude carbazole from petroleum residues was impossible up to the time of the application of chromatography, and even with this technique it is a difficult problem. Various methods of purification have been described in the literature, some of which will be dealt with in a later section. In so far as melting points may be used as criteria of purity, various figures have been quoted ranging from 238°C[77,78] in old papers, to the currently accepted value for the pure synthetic material of 246°C.

The formation of carbazole pyrogenically has been reported by Graebe who passed aniline[79] and diphenylamine[80] vapour through a red hot porcelain or iron tube. It has similarly been obtained using methyldiphenylamine[81] and 2-amino-diphenyl.[82] Graebe reported that carbazole itself may be passed through a red hot tube without decomposition.[83]

The work to be described deals with the pyrolysis of carbazole in the hope of determining the strength of the N.H bond in carbazole, in a manner analogous to that employed in the previous section of this thesis.

Practical aspects of the determinations of the N.H.

bond strength have been reported; in the case of ammonia there is data by Glockler[84], Richards[85], and Szwarc[86] and the pyrolysis of hydrazine and benzylamine has been used by Szwarc[86] to obtain values for the heat of formation of the $-NH_2$ radical.

The pyrolytic decomposition of ammonia had to be abandoned by Szwarc. The use of toluene as carrier gas in the pyrolysis of hydrazine allowed the NH_2 radicals to be quickly removed from the reaction by the benzyl radicals according to the equation

$$PhCH_3 + NH_2 \longrightarrow PhCH_2 + NH_3$$

The benzyl radicals dimerised. The rate of formation of dibenzyl was used as a measure of the rate of decomposition of the hydrazine. Some hydrazine decomposed heterogeneously forming N_2, H_2 and ammonia, but since dibenzyl was not formed proportionately it was suggested that NH_2 radicals were produced by a homogeneous, first order mechanism, the velocity constant of which was in accord with the following

$$k = 4 \times 10^{12} e^{-60 \pm 3/RT}$$

Only 2% of the total decomposition at 660° was by a homogeneous reaction and 30% at 780°C. The energy of activation is considered to be that of the decomposition.

$$N_2H_4 \longrightarrow 2NH_2$$

When benzylamine was similarly pyrolysed, dibenzyl was produced equimolecularly with ammonia. The rate equation was found to be $k = 6 \times 10^{12} e^{-59.4/RT}$ where the energy of activation was taken to correspond with the reaction

$$PhCH_2NH_2 \longrightarrow PhCH_2 + NH_2$$

These dissociation energies lead to the value 104 K.cals. for the dissociation of the first N-H bond in ammonia.

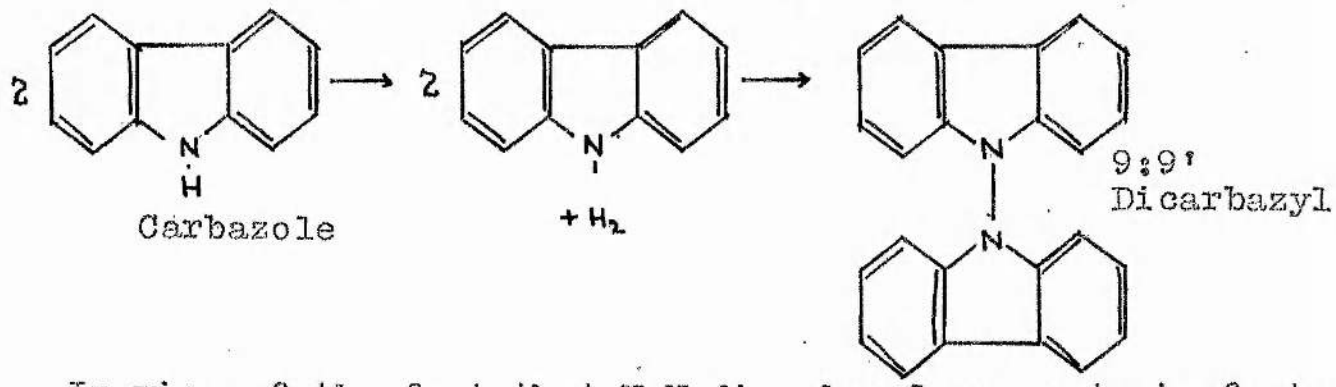
In considering the possibilities in the pyrolysis of carbazole it is relevant to review some general chemical facts indicating the reactivity of various positions in the ring system.

In the carbazole molecule, the hydrogen atom attached to the heterocyclic nitrogen may be replaced by the most strongly electro-positive metals or by radicals. Treatment with fused caustic potash yields potassium carbazole, which on further heating, produces KCN. N. benzyl and N.acetyl carbazoles are formed by treatment with the appropriate acid chloride and anhydride respectively.

The oxidation of carbazole with permanganate is interesting and has been most exhaustively investigated by McLintlock, Perkin, and Tucker[87,88], the crystallography of the products being studied by Porter.[89] Three products were obtained, N.N dicarbazyl, 3.3' dicarbazyl, and a mixture of other types of dicarbazyls. It is not considered that these are the primary products of the oxidation, however.

The oxidation of diphenylamine with sodium dichromate in glacial acetic acid yields diphenyl benzidine[90], and it is well known that the hydrogen atoms at the 1 and 3 positions of carbazole are susceptible to substitution. Several instances are known of groups migrating from the N of the imide group to either of these positions, for example, under certain conditions of temperature, the potassium salt of carbazole N.carboxylic acid breaks down to give carbazole 1 carboxylic acid.[91] Wieland[92] has shown that in the chromic acid oxidation of diphenylamine, tetraphenylhydrazine is first formed, and the acid medium then converts this, by intramolecular rearrangement, to diphenylbenzidine.

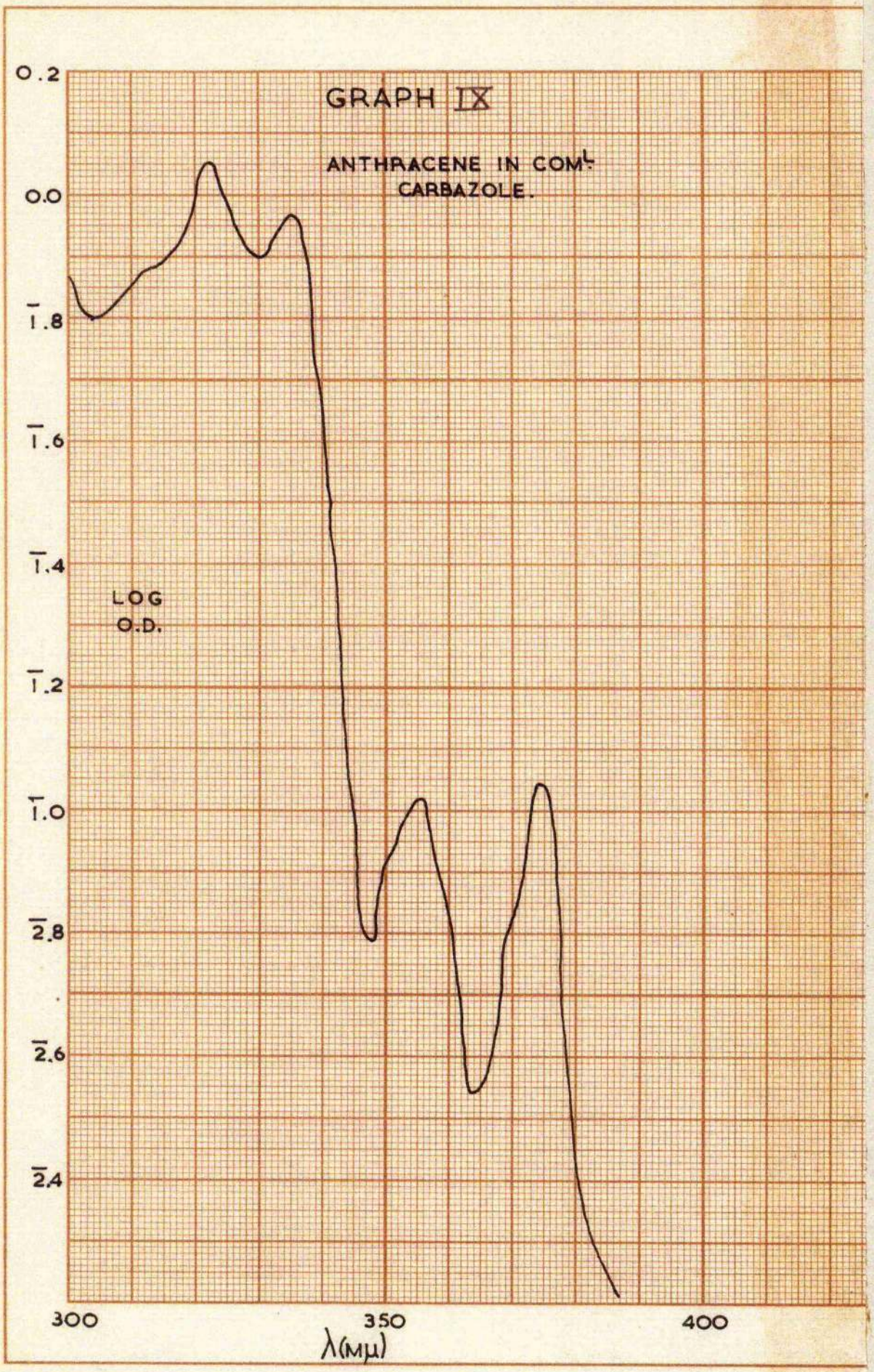
These considerations, taken in conjunction with the work done on the pyrolyses of diphenylmethane and fluorene, made the thermal decomposition of carbazole appear to be a suitable subject for study, since the following reaction sequence appeared probable at high temperature.



Carbazole

9:9' Dicarbazyl

In view of the fact that N.N dicarbazyl was not, in fact, the principal product and to preserve continuity throughout the section, the work done will be considered as a whole,


GRAPH IX
ANTHRACENE IN COML. CARBAZOLE.
0.2
0.0
$\bar{1}$.8
$\bar{1}$.6
$\bar{1}$.4
$\bar{1}$.2
$\bar{1}$.0
$\bar{2}$.8
$\bar{2}$.6
$\bar{2}$.4
LOG O.D.
300
350
400
λ(mμ)

rather than be treated in chronological order.

Preparation of compounds used.

Carbazole.

Commercial carbazole, obtained from coal tar, was available.

The purification of such material, however, is an extremely difficult matter and innumerable methods for doing this appear in the literature. They consist, essentially, of removing impurities by specific solvents and making use of the low solubility of carbazole itself; this method is now acknowledged to be unsatisfactory and not capable of producing absolutely pure carbazole. A sample of commercial carbazole was examined on the U.V spectrophotometer and its absorption is shown on Graph IX. It is seen that anthracene was present to the extent of 5%.

A variety of synthetic methods is available, utilising as starting material triazole[93], dicyclohexylamine[94] and tetrahydrocarbazole[95]. Of these, tetrahydrocarbazole seemed the most suitable compound and two methods were applied for its preparation. Equimolecular amounts of cyclohexanone and phenylhydrazine were mixed, and 50 gms. of the resulting phenylhydrazone were then shaken for four hours in the cold with 500mls. 20% sulphuric acid. The product was filtered, washed and recrystallised. An overall yield of 70% was recorded. A more satisfactory method[96] is to add phenylhydra-

zine to a mixture of acetic acid and cyclohexanone boiling under reflux.

1 mole cyclohexanone and 6 moles acetic acid were placed in a 1 litre 3-necked flask fitted with stirrer, reflux condenser and tap funnel. When boiling, 1 mole phenylhydrazine was added through the tap funnel during 1 hour, and boiled for a further hour. The product was collected and purified by recrystallisation. A yield of 90% of product melting at 118°C was recorded.

Dehydrogenation of various substituted tetrahydrocarbazoles may be carried out by chloranil[97] in very high yields. Chloranil may be prepared by the electrolytic oxidation of aniline[98], perchlorate oxidation of aniline or phenol[99], or by treating 1:4 benzoquinone in acetic acid with chlorine[99]. A perfectly pure product can be obtained most simply by the action of a 2:3 mixture by volume of nitric and hydrochloric acids on hydroquinone[100] and this method was employed. Unfortunately, the material gave very poor yields indeed and despite repeated attempts, no improvement could be made.

The most satisfactory technique was the use of palladised charcoal. 10% Pd/C was prepared by the normal method of treating with hydrogen a mixture of palladium chloride in a suspension of specially purified charcoal.

30% Pd/C was prepared by carrying out the reduction of the palladium with formaldehyde. Either product effected

a very speedy dehydrogenation and 50 gms. of tetrahydrocarbazole could be reduced in about 45 minutes at 220°, a Wood's Metal bath being used to heat the reaction flask. The product was extracted with methanol and perfectly pure white, crystalline plates were obtained, melting at 246°C. Since carbazole is of extremely low solubility in all solvents except acetone, it was found convenient to extract the material with acetone from a flask fitted with an internal syphoning device so that the boiling solution could be transferred to an electrically heated filter funnel. The crystals obtained in this way were then purified from methanol as required.

9.9' Dicarbazyl.

The method of Perkin and Tucker[87] was employed. 2 litres of acetonewere refluxed with potassium permanganate until the red colour persisted. The acetone was then distilled, dried, and redistilled. 100 gms. carbazole were added to 700 gms. acetone and boiled under reflux. Two separate portions of 50 gms.powdered permanganate were added to the boiling mixture giving a vigorous reaction. After refluxing for some hours, the permanganate colour was almost discharged. When the precipitate had settled it was filtered and extracted with boiling acetone. The combined acetone extracts were then evaporated to dryness and the residue dissolved in boiling benzene, filtered, and allowed to crystallise. Only the first crop of crystals was taken off and purified, the final

product having a constant melting point at 221°C. On further evaporation of the liquors, crystals of the 3:3', 1:1', and 3:9' dicarbazyls were obtained and identified by their melting points.

9:10 dihydro 9:10 diphenyl phenazine.

N.nitroso diphenylamine was made by the standard method of adding powdered sodium nitrite to a mechanically stirred ice-cold solution of diphenylamine in hydrochloric acid. A pure product, melting at 66.5° C was readily obtained in quantitative yield. The conversion of this compound to the phenazine was achieved by modifying the method of Wieland,[101] a solution in toluene being refluxed in a stream of carbon dioxide. The exit gases were bubbled through a 40% solution of caustic potash followed by tared bubbling tube filled with saturated ferrous sulphate, the inlet and outlet tubes being attached to calcium chloride drying tubes. After a certain time the absorption unit was removed and weighed and hence the rat of generation of nitric oxide was calculated. The reaction was complete after 30 hours. A second decomposition of the nitroso compound was carried out by heating the compound in the dry state in a current of carbon dioxide. The technique was basically the same as the previous experiment except that the carbazole produced in the reaction sublimed and so a partial purification of the phenazine was achieved. The melting point of the ultimate product was 172°C.

Carbazole analogue of the previous compound.

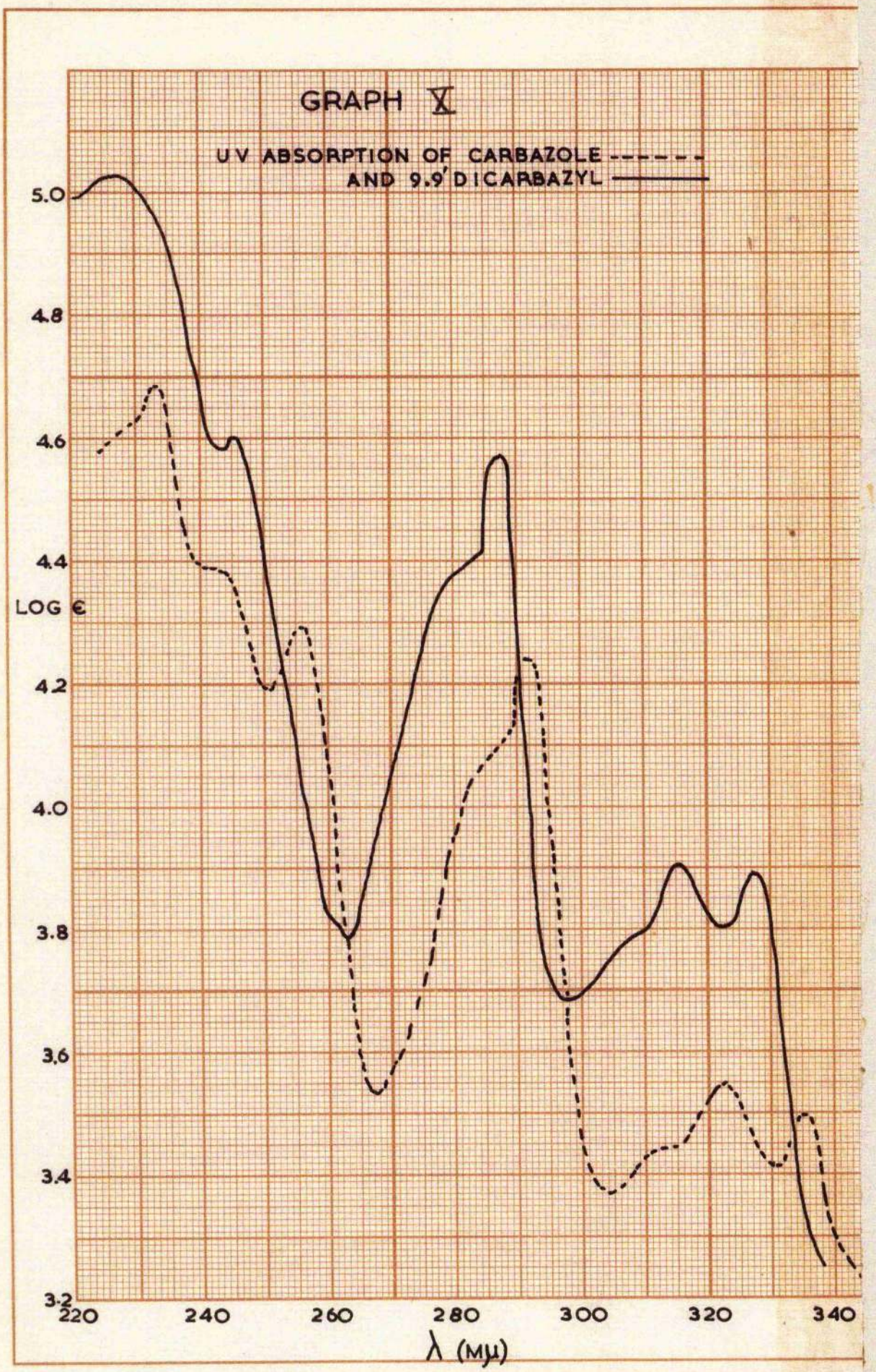
Since diphenylamine can be transformed to the phenazine described above, consideration of the stereochemistry of diphenylamine and carbazole suggested that the phenazine formation would be even readier in the case of carbazole. N.nitroso carbazole was prepared by the method of Wieland and Susser.[102] 17 gms. of carbazolewere dissolved in 250mls. of boiling acetic acid and the solution allowed to cool slightly. At the point of incipient crystallisation the solution was mechanically shaken and small portions of a saturated aqueous solution of sodium nitrite were added. The mixture was then cooled thoroughly and diluted with water. The nitroso compound was filtered and purified.

Decomposition of this compound was effected by both the methods applied to nitroso diphenylamine and, in addition, it was pyrolysed by the technique employed for carbazole. This decomposition will be dealt with in a later section.

The final product could not be isolated in a pure state and the only way that information could be obtained was by putting the completely decomposed system i.e. the residue when nitric oxide ceased to be evolved, through a chromatographic column and doing ultra violet absorption determinations on fractions of the eluate.

Quantitative Analysis of Mixtures of Carbazole and N.N Dicarbazyl.

In the pyrolysis of fluorene[2] the main products were found to be difluorenyl, hydrogen, and very small amounts of bis-


GRAPH X
UV ABSORPTION OF CARBAZOLE ------
AND 9.9' DICARBAZYL ——
5.0
4.8
4.6
4.4
LOG €
4.2
4.0
3.8
3.6
3.4
3.2
220
240
260
280
300
320
340
λ (Mμ)

diphenylene ethylene. The nitrogen atom in carbazole is trivalent and so no nitrogen analogue of bis.diphenylene ethylene could be formed; instead, the sole product was expected to be N.N dicarbazyl. Before starting the pyrolytic work an investigation was made into methods of estimating this probable product of reaction in the presence of a large excess of carbazole.

Preparation of Standard U.V. Data.

Standard solutions of carbazole and dicarbazyl were made up in methyl alcohol and examined on the spectrophotometer. The data obtained are shown graphically on Graph X. The technique employed was precisely similar to that described in the triphenylmethane section (page 51).

Synthetic mixtures of carbazole and N.N dicarbazyl were prepared in the concentrations anticipated from actual runs and techniques of analysis investigated.

Method 1. Method of simultaneous equations from the U.V. absorption of mixtures.

From the curves given for carbazole and dicarbazyl on Graph X it is seen that at 322, 304, 284 and 244mμ the value of $d(\log \epsilon)/d\lambda$ is a minimum or zero, hence these wavelengths appeared suitable for applying this method.

In the first analysis the concentrations of carbazole and dicarbazyl were, respectively, 157×10^{-6} and 8.9×10^{-4} moles/litre. The results obtained are given in tables 10 a, b,

- -

Analysis of mixtures of Carbazole and N-N Dicarbazyl.

Table of results obtained by direct analysis of mixture on U.V. Spectrophotometer.

Table 10a.

Solution	Sample.	Optical Densities.			
		322mμ	304mμ	284mμ	244mμ
1	a	.621	.373	.379	.407
	b	.616	.416	.401	.410
2	c	.675	.453	.438	.442
	d	.674	.456	.434	.451
	e	.680	.454	.434	.453

a and b were duplicates of one mixture: c, d and e were triplicates of another mixture.

Table 10b.

Results of solution of equations:

	a		b		c		d		e	
λ_1 λ_2	[C]	[D]	[C]	[D]	[C]	[D]	[C]	[D]	[C]	[D]
322 304	139	18.7	-		172	0.89	1.67	1.16	176	0.74
322 284	137	19.6	139	19.8	154	1.90	1.58	1.67	167	1.26
322 244	143	16.5	168	18.9	161	1.51	-		188	0.62
304 284	150	14.1	-		-		1.71	1.04	-	
284 244	139	18.9	144	16.6	157	1.77	-		175	0.90
304 244	140	18.0	-		168	1.20	1.76	0.77	181	0.51
Average:	141	17.6	141	17.7	162	1.19	1.68	1.16	177	0.81
Actual:	157	8.9	157	8.9	164	1.23	1.65	1.23	164	1.23

[C] = 10^6 x concentration of carbazole.

[D] = 10^6 x concentration of dicarbazyl. moles/litre.

where optical densities are recorded, and which shows the results obtained by solving equations derived from the optical densities at 322, 284 and 244mμ. The optical densities at 304mμ gave negative values for the dicarbazyl concentration.

Since the composition of the solution made up from run products could alter by varying reaction conditions, a second synthetic mixture of 164 x 10^{-6} moles carbazole/litre and 1.23 x 10^{-6} moles dicarbazyl/litre was prepared. Results of triplicate analyses are given in the same tables.

Assessing the accuracy of the spectrophotometer at ±2%, leading to an accuracy of results of ±10% showed that at best this method could only be used as a preliminary check of concentrations.

Method 2 Chromatography.

Reference is made in standard textbooks to the purification of anthracene from mixtures of this substance with carbazole. A solution in n-hexane deposits the carbazole at the top of an alumina column, the anthracene being carried down the column by the solvent action of further quantities of pure hexane.

Experiment 1.

A mixture of carbazole and dicarbazyl in hexane solution was percolated through an alumina column, Fractions of eluate were examined on the spectrophotometer using method 1

for the analysis and from the results obtained it was clear that only a partial separation was being achieved. The dicarbazyl did, however, appear to be rather more soluble in hexane whereas the highest dicarbazyl concentrations occurred in earlier fractions, succeeding fractions revealed a gradually increasing proportion of carbazole.

n-hexane was considered unsuitable for the separation.

Experiment 2.

The second solvent used was the 60° - 80° fraction of petroleum ether. After applying the solution to the column and eluting with further quantities of petroleum ether, two fluorescent bands were observed in U.V. light.

The bands were separated by elution with a 5% solution of hexane in petroleum ether and the column was extruded, the material in the bands being extracted by refluxing with methyl alcohol. U.V. examination, however, showed that only a partial separation of the components had taken place.

It appeared from these two experiments that a chromatographic technique was going to be unwieldy, although it was probable that a complete separation could ultimately be achieved.

Experiment 3.

100 mls. of petroleum ether was saturated with carbazole and dicarbazyl by refluxing over the solid products for one

hour. After cooling, the solution was filtered and poured on a column of alumina. The first portion of eluate fluoresced strongly in U.V. light; after concentrating, crystals of pure dicarbazyl were collected. Identification was by melting and mixed melting point, and also by U.V. absorption.

Two sections of the column were cut out, one being fluorescent. These were refluxed over methyl alcohol and the extracts transferred to the cells of the spectrophotometer. With the non-fluorescent sample as 'solvent' and the other as 'solution', a curve for pure carbazole was obtained. It was inferred, therefore, that the concentration of dicarbazyl in both cells was the same.

This experiment indicated the nature of the technique finally adopted.

Method 3. Principle of Differential Absorption.

The "solvent" cell of the spectrophotometer was filled with methyl alcohol, the other with a solution of carbazole and dicarbazyl. The addition of drops of pure dicarbazyl in methyl alcohol to the solvent cell allowed the spectrum of pure carbazole to be obtained, when the concentration of dicarbazyl in both cells was equal.

The epsilon values for pure carbazole were noted at two maxima (322 and 335mμ) and the ratio obtained. With unequal concentrations of dicarbazyl in the cells, this ratio was not found.

Table 11a.

Analysis of mixture of carbazol and dicarbazyl by balancing out absorption due to dicarbazyl.

Solution: Carbazol : .0001317 mole/l.
Dicarbazyl : .0000489 mole/l.

For pure carbazol.

ϵ_{335} = 3160

ϵ_{322} = 3589

Ratio = 0.878

Drops dicarbazyl solution added to solvent cell.	O.D. 335	O.D. 322	Ratio	Change in ratio/drop.
0	.470	.782	.601	-
10	.448	.667	.672	.007
12	.432	.572	.755	.008
15	.408	.471	.866	.0073
1.5	.407	.464	.877	.0073

Result of analysis:
Carbazole : .000128 mole/l. (2.3%).
Dicarbazyl : .0000491 mole/l. (0.4%).

Table 11b.

Solution used: Carbazole : .000155 mole/l.
Dicarbazyl : .00000357 mole/l.

Drops dicarbazyl solution added to solvent cell.	O.D. 335	O.D. 322	Ratio	Change in ratio/drop.
0	.497	.602	.825	-
4	.491	.574	.855	.0075
$2\frac{1}{2}$	.483	.552	.875	.008
$\frac{1}{2}$	.482	.546	.880	.01

Hence - Carbazole : .000152 (1.98%).
Dicarbazyl : .00000370 (7.3%).

Proof of this technique was obtained by the following procedure.

A mixture of 10 mls. carbazole solution (0.082 g.p.l.) and 4.95 mls. dicarbazyl (0.082 g.p.l.) was made up to 25 mls. (solution A.) 4.95 mls. dicarbazyl solution was diluted to 25 mls. (solution B.) Solutions A and B had thus the same concentration of dicarbazyl.

B was considered as solvent and A as solution in the cells of the spectrophotometer. A curve for carbazole was obtained. B was then rejected and the cell refilled with methanol; the optical densities were then measured at 322 and 335 mμ and the ratio calculated. On the addition of drops of dicarbazyl to this solvent cell, the ratio gradually increased, the change of ratio per drop added being, surprisingly, proportional to the number of drops added. It was possible, in fact, to calculate the number of drops necessary in any particular analysis.

When the required ratio of optical densities was obtained, solution A was rejected and the cell refilled with methanol. The concentration of dicarbazyl was then obtained in the usual way. The results of two of the experiments carried out are given in tables lla and b.

Survey of decomposition products.

Several runs were carried out in order to accumulate solid products for chromatographic analysis; information was meantime obtained about the volatile products.

Hydrogen was detected on the mass spectrometer, being estimated both on this instrument and by combustion in the gas measuring system. This latter technique showed that another gas was present which from its failure to condense in liquid air or burn was deduced as methane. Confirmatory mass spectrometric evidence was obtained.

In a preliminary run carried out at 865°C, 14.1×10^{-4} moles carbazole were passed through the furnace. The gaseous products were collected in the gas measuring system, the hydrogen being burned. On transferring the residual products to the handling system of the mass spectrometer the following voltage increases were observed:

Mass.	2	15	16	28	32	44	
Background.	109	.04	.09	.2	.09	.05	volts.
Sample.	.12	7.4	8.3	15.0	.07	.05	"

The ratio of the increase in mass 16 to mass 15 voltages was 1.11 (Methane 1.25). The amount of hydrogen was 4.08×10^{-5} and of methane 0.17×10^{-5} moles.

A second run with the furnace at 776°C was carried out with the mass spectrometer as part of the flow system. This run, lasting some six hours at the low temperature with a short time of contact yielded the following data:

Moles carbazole = 55.1×10^{-3}

" H_2 = 6.56×10^{-5}

" CH_4 = 1.32×10^{-5}

An investigation of the higher mass range was made on the

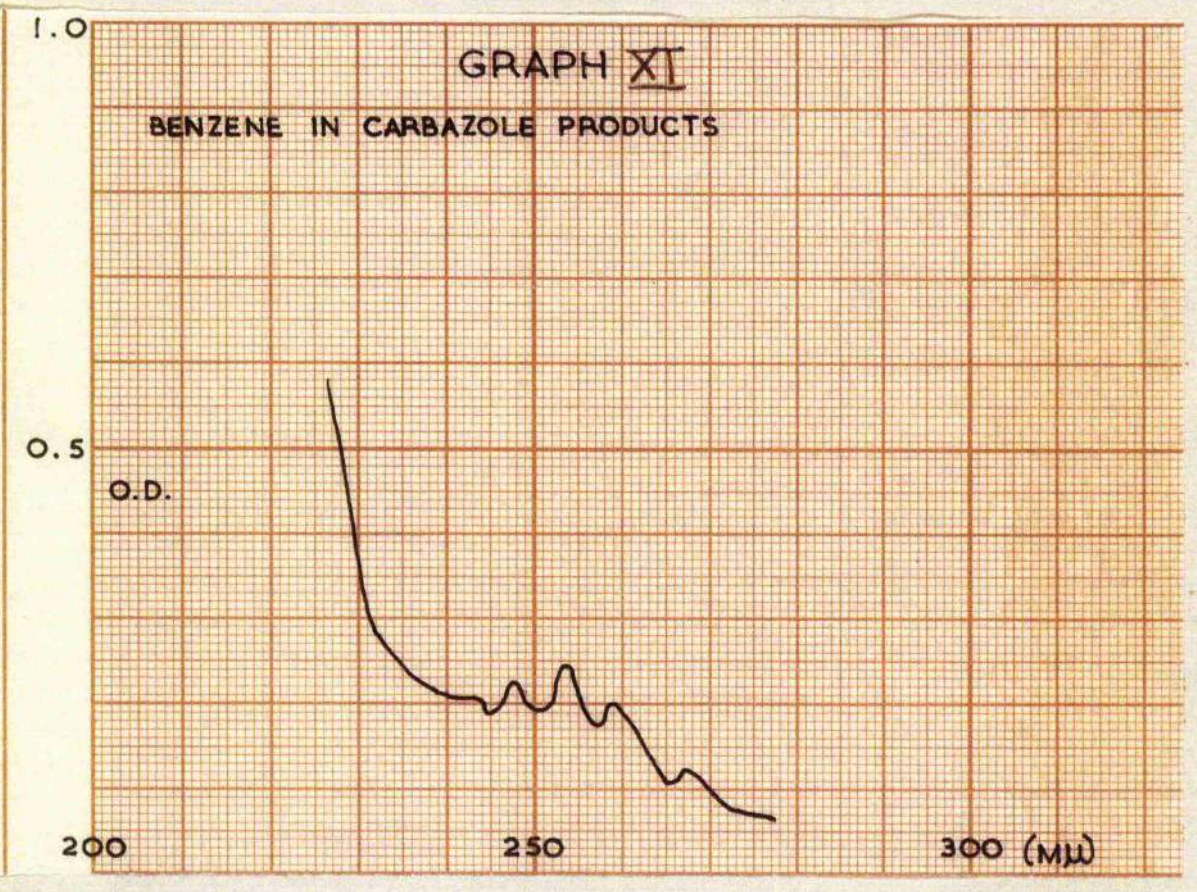
mass spectrometer. The contents of the liquid air trap at the furnace exit were distilled in two stages into two small vessels which were made by blowing a bulb on one limb and a cone on the other of a right angled tap. The vessel could thus be attached to the pyrolysis apparatus, the distillation carried out, and the tap closed. The contents were then expanded into the handling system of the mass spectrometer.

The distillations were at -80° and -40°C. Complete mass spectra from m/e 100 down were made and the following alterations in peak heights were noted:

Mass No.	Increment in recorded voltage (m V).	
	-80°	-40°
92	0	262
91	2.5	425
78	58	218
77	8.5	47.5
65	1.0	18.0
52	24.3	54.0
51	34.3	88.0
27	416.0	
26	482.0	

The sample collected at -80°C was distilled over KOH and re-injected to the mass spectrometer. The new increments in voltage of masses 26 and 27 were 0.87 and 0.75mV respectively. Since the odour of HCN had been noted previously this evidence is taken as confirmation of the presence of the compound. An attempt to calibrate the mass spectrometer with HCN was abandoned as unduly hazardous.

The results quoted were taken in two groups; one group


GRAPH XI
BENZENE IN CARBAZOLE PRODUCTS
1.0
0.5
O.D.
200
250
300 (MU)

was recalculated to take mass 91 as 100% and the other for mass 78 to be 100%. The other peak heights were then compared with published data[103] and prove the existence of benzene and toluene.

	Mass	Voltage	Literature data
Toluene.	92	61.5	80
	91	100	100
	65	16	14.2
	63	10.7	9.5
	51	20	10.3
Benzene.	79	7.3	6.5
	78	100	100
	77	21	14
	52	25	19.2

The contents of the two vessels were then dissolved in methanol and analysed on the spectrophotometer. Graph XI is confirmation of benzene but toluene could not be detected in this way.

The mass spectrometer was calibrated with benzene and toluene by the use of micro burettes and the quantities involved in the experiments determined.

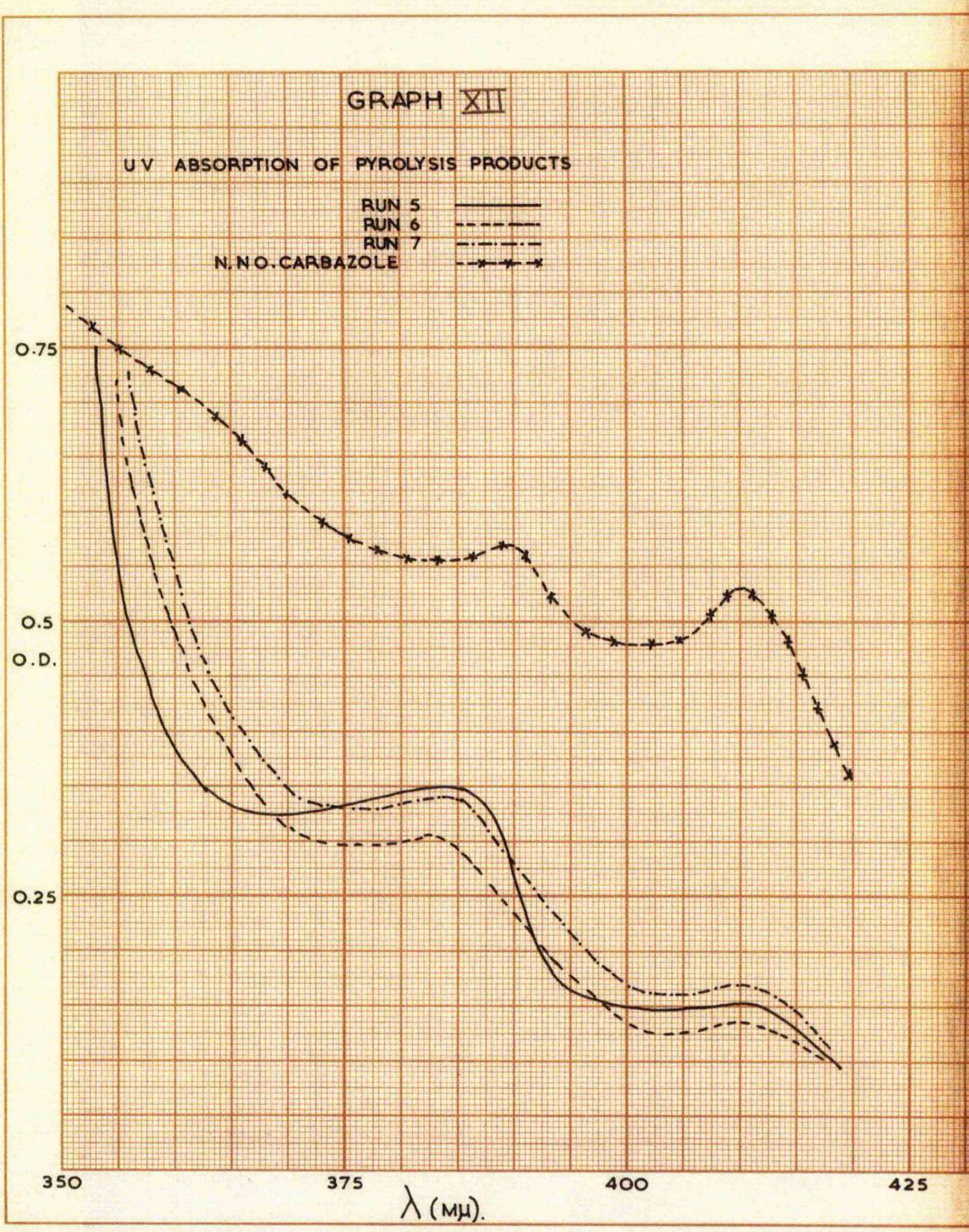
Moles carbazole. = 6×10^{-3}

" H_2 = 4.2×10^{-5}

" C_6H_6 = 0.4×10^{-5}

" $C_6H_5CH_3$ = 0.8×10^{-5}

Carbon formation was measured by passing 1 gram of carbazole through the reactor at 775°. Oxygen was later admitted to the apparatus and the CO_2 formed condensed in a liquid air trap; it was then expanded into the mass


GRAPH XII
UV ABSORPTION OF PYROLYSIS PRODUCTS
RUN 5
RUN 6
RUN 7
N.NO.CARBAZOLE
0.75
0.5
O.D.
0.25
350
375
400
425
λ (mμ).

spectrometer, the results are given below indicating a decomposition of 0.6%.

Moles carbazole = 6×10^{-3}

" H_2 = 6×10^{-5}

" CO_2 = 4.8×10^{-4}

The experiment was carried out in a clean furnace and this point will be dealt with further.

An exhaustive search for aniline was unsuccessful.

Solid products.

The contents of the trap at the furnace exit were dissolved in methanol and the absorption from 220 to 700mμ determined. None of the results corresponded with N.N dicarbazyl; absorption maxima were, however, observed at 386 and 412mμ as shown by the three runs on graph XII.

The examination of chromatographic fractions failed to show any trace of the dicarbazyl.

A proportionality was noted between the amount of hydrogen formed and the optical density at 386mμ in two sets of three identical runs. Carbon had been observed to form on the silica furnace and each set of runs was carried out without allowing access of air to the hot furnace. After each 'first' run, therefore, the furnace was coated with carbon.

Three traps were fitted to the furnace exit; the product of the first run was flamed gently from the trap nearest to, to

the trap furthest from the exit. This resulted in some further decomposition of material as evidenced by an involatile residue left behind.

The results obtained were as follows:-

Run	Temp. °K	Volts H_2	O.D. 386mμ
21	1101	0.78	0.216
22	1101	0.59	0.400
23	1100	0.68	0.582
24	1092	0.52	0.153
25	1092	0.36	0.267
26	1092	0.30	0.230

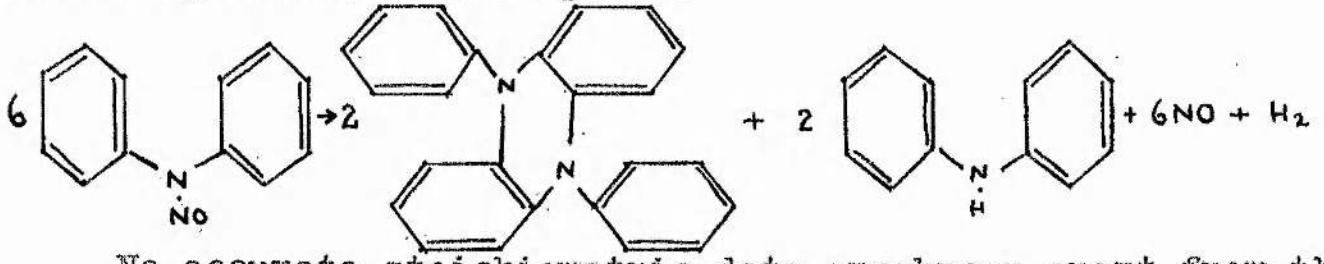
$V_{H_2}(22)/V_{H_2}(23) = 0.868$ O.D.(22)/O.D.(23) = 0.867

$V_{H_2}(25)/V_{H_2}(26) = 0.830$ O.D.(25)/ O.D.(26) = 0.861

Coating the inside of the furnace with barium chloride gave similar results in that the first of a set of runs gave an abnormally high amount of hydrogen.

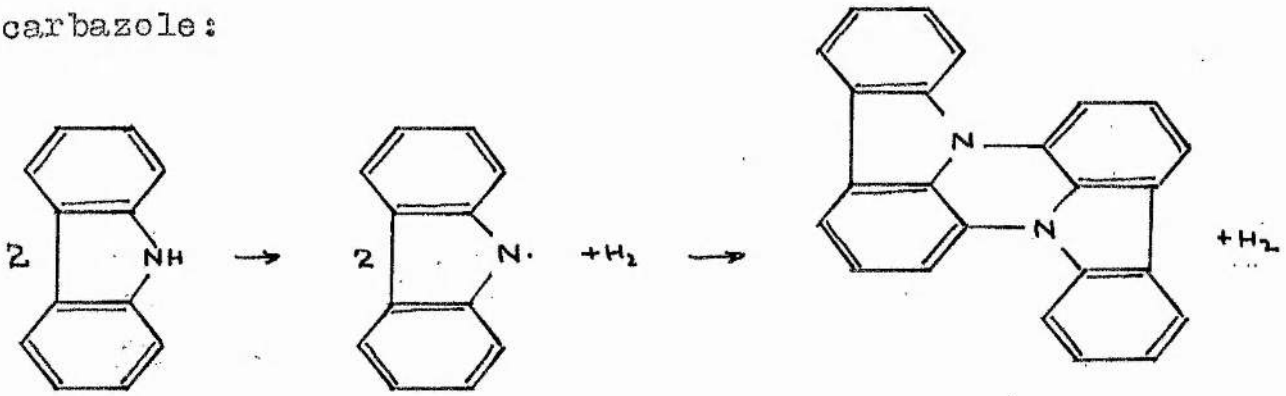
Since no dicarbazyl had been produced it was necessary to speculate upon possible reaction products. From the literature it became apparent that a possible radical combination could lead to the formation of a phenazine type of compound.

When N-nitroso diphenylamine is heated either in the dry state or refluxed over toluene for 48 hours, the following reaction takes place:



No accurate stoichiometric data are known apart from the

fact that approximately equal amounts of the phenazine and diphenylamine are produced. The formation of the phenazine is almost certainly the result of a radical combination and hence the following scheme is possible for the pyrolysis of carbazole:



The ultimate product is a phenazine; an alternative name is 1:9-9':1' dicarbazolene. This material shows absorption maxima at the same wavelengths as the reaction product of carbazole. The pure material was not prepared since its purification would have been identical with that needed for the run products.

The very small amount of material available made purification difficult and so calculations were made to compare the molar yields of phenazine and hydrogen, the phenazine being estimated from the published data.[104]

Run	Temp °K.	Moles H_2	Moles phenazine.
5	1098	0.09×10^{-5}	0.12×10^{-5}
6	1092	$.19 \times 10^{-5}$	$.09 \times 10^{-5}$
7	1088	$.09 \times 10^{-5}$	$.20 \times 10^{-5}$

The agreement is not very good. This substance, however, was the only material detected in the solid product after a most

exhaustive chromatographic analysis, which will be detailed later.

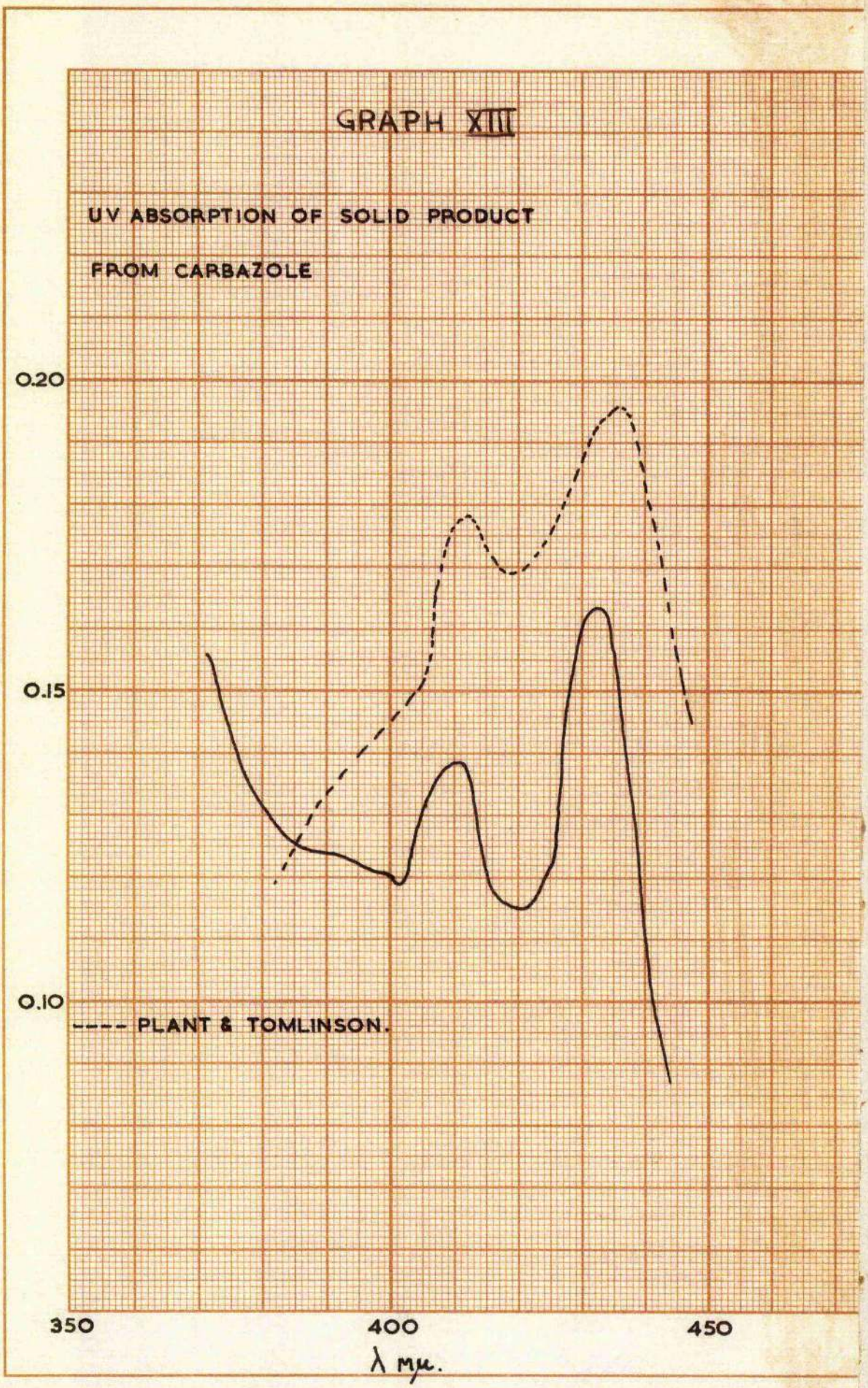
Runs to accumulate kinetic data were carried out and the solid products retained and bulked for analysis. The decomposition was measured by hydrogen formation.

To preserve continuity of reporting, the work done on the solid products is being continued. A fraction cutter was devised and constructed; the constructional details are given as an appendix to this thesis.

A known weight of N-nitroso carbazole was placed in a porcelain boat in the inlet lead to the furnace. The boat was warmed gently and, after some practice, it was found possible to admit the material at a reasonable rate to the furnace. A green product, in appearance the same as that obtained from carbazole, was observed in the exit trap. After partial purification by sublimation, the U.V. absorption of this green substance was determined. The result is included on graph XII.

Chromatographic separation of the product from carbazole.

As stated previously, n-hexane has been used in the purification of commercial carbazole by chromatography on alumina. Carbazole itself is not fluorescent, but when a solution in hexane is applied to the column, fluorescent bands due to impurities, [illegible] generally compounds of higher molecular weight such as anthracene, phenanthrene, etc., are observed.


GRAPH XIII
UV ABSORPTION OF SOLID PRODUCT
FROM CARBAZOLE
0.20
0.15
0.10
---- PLANT & TOMLINSON.
350
400
450
λ mμ.

Pure carbazole was dissolved in various solvents and mixtures of solvents. Each solution was applied to a column and each fraction of eluate was evaporated to dryness and weighed. Data were thus accumulated on the behaviour of the substance, and the main analysis was carried out on the basis of these data with the following as solvents:

1. n-hexane.
2. 2½% methanol in hexane.
3. 25% benzene in hexane.
4. benzene.

184 fractions were taken from the column and the fractions taken in groups of five for evaporation, and U.V. analysis of each residue in methanol.

The initial absorption of the product mixture was as shown in graph XII and the final plot is given on graph XIII where there is also the literature curve[104] for the product in the region of the wavelength used. It was not possible to remove the last traces of carbazole and hence the absorption below 340mμ included a contribution from the carbazole. Graph XII includes the absorption of the green material obtained from the N-nitroso carbazole.

The evidence detailed indicates that the product from carbazole which is formed in near equimolecular proportion with hydrogen is the substance described by Plant and Tomlinson[104] as 1:9-9':1' carbazolylene.

Table 12.

Calibration of Injector Unit with Carbazole.

Boiler Temp.	Valve delivery Moles carbazole/ minute.	Average deliveries.
218°C (Benzylacetate 760 m/m)	.000148 .000153 .000148	.000149
224°C (Methyl salicylate 760m/m)	.000171 .000173 .000175 .000173 .000177	.000174
234°C (Benzophenone 14.5 m/m) 234°C (Carvone 723m/m)	.000368 .000378 .000375	.000374


GRAPH XIV
VAPOUR PRESSURE OF CARBAZOLE
150
V.P.
(MMS)
100
50
0
200
250
300
TEMP. °C.

Kinetic Data on Reaction.

From the survey made of the nature of the products there seemed a possibility that an investigation of the kinetics of formation of hydrogen might be profitable. For this purpose it was essential to have a reproducible injection system and the following section describes the calibration of the injector unit shown on diagram 2.

Calibration of injector.

Pure carbazole was transferred to the container of the unit and degassed by the same technique detailed in the triphenylmethane section. Since carbazole has a much higher melting point, it was not possible to melt the material in vacuo so the material was degassed in the solid state. Data were obtained on the vapour pressure of carbazole, graph XIV showing the variation with temperature. Phenyl ethyl alcohol (boiling point 220°C) was selected as container heating liquid in the preliminary runs.

The experimental technique was precisely similar to that described in the previous section of the thesis, the only exception being that all the leads through which carbazole passed were maintained at 250°C to prevent condensation of the vapour.

Calibration data are given in table 12.

Variations of reaction conditions.

The kinetic data on the decomposition of carbazole were

GRAPH XV

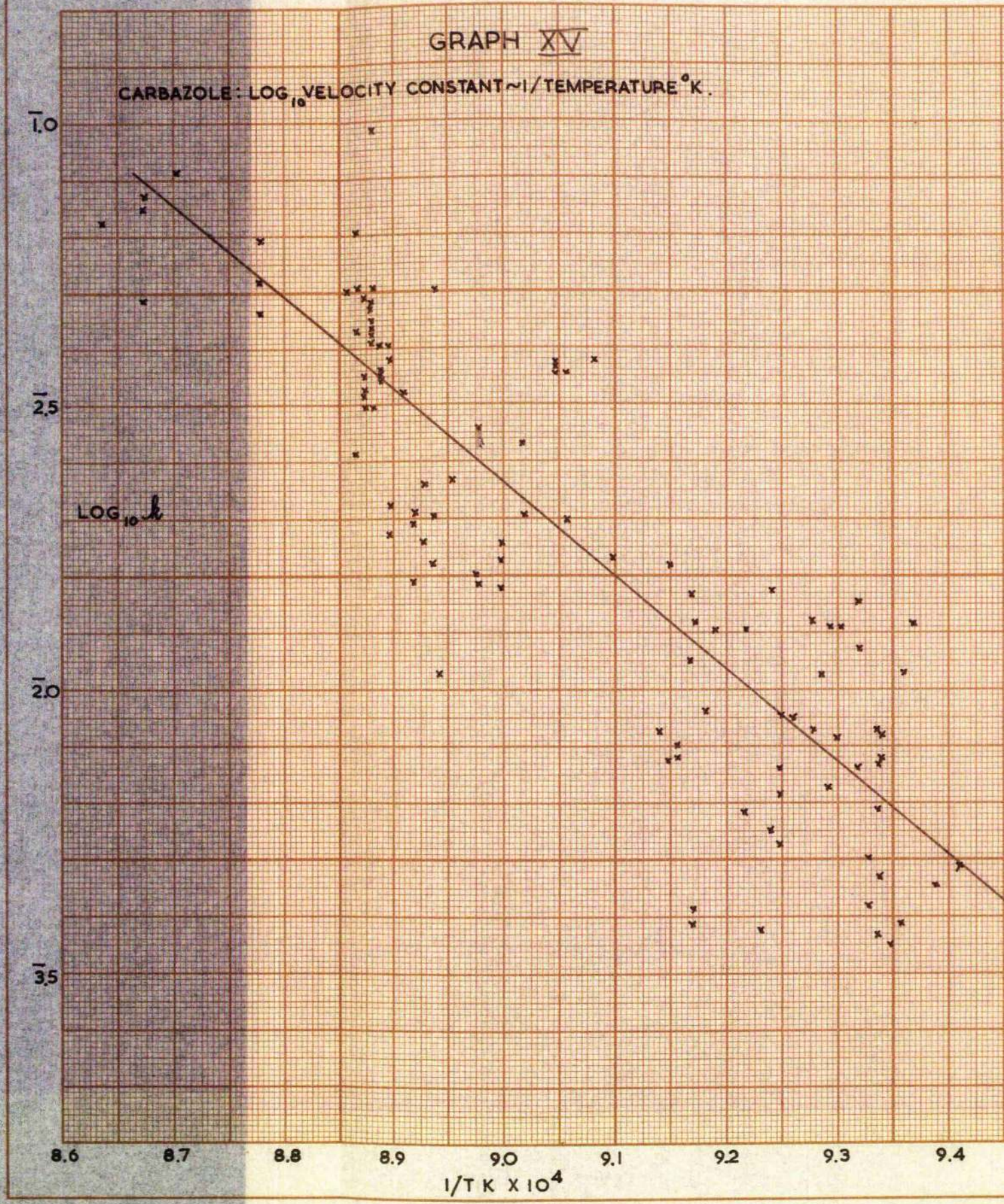

CARBAZOLE: LOG10 VELOCITY CONSTANT ~ 1/TEMPERATURE °K.
$\bar{1}.0$
$\bar{2}.5$
$\bar{2}.0$
$\bar{3}.5$
LOG10 k
8.6
8.7
8.8
8.9
9.0
9.1
9.2
9.3
9.4
1/T K X 10^4

Table 13.

Variations of reaction conditions.

(i) Partial pressure of carbazole.

Run	Temp. ^{o}K.	pp.mm.	k. sec^{-1}
48	1127	.286	.0339
106	1127	.674	.0336
52	1114	.214	.0141
123	1114	.99	.0148

(ii) Time of contact.

Run	Temp. ^{o}K.	t.(secs.)	k. sec^{-1}
42	1072	.493	.0049
68	1072	.858	.0051
112	1124	.267	.0198
168 (P)	1124	.853	.0186

distinctly disappointing. It was not found possible to obtain that degree of reproducibility that makes the checking of rate equations an easy matter. The variations are most readily seen at a glance by considering graph XV where the logarithms of first order constants are plotted against the reciprocal of the absolute temperature. Quite clearly the range of log k values, which are not associated in any regular way with variations in reaction conditions, ~~are~~ is considerable.

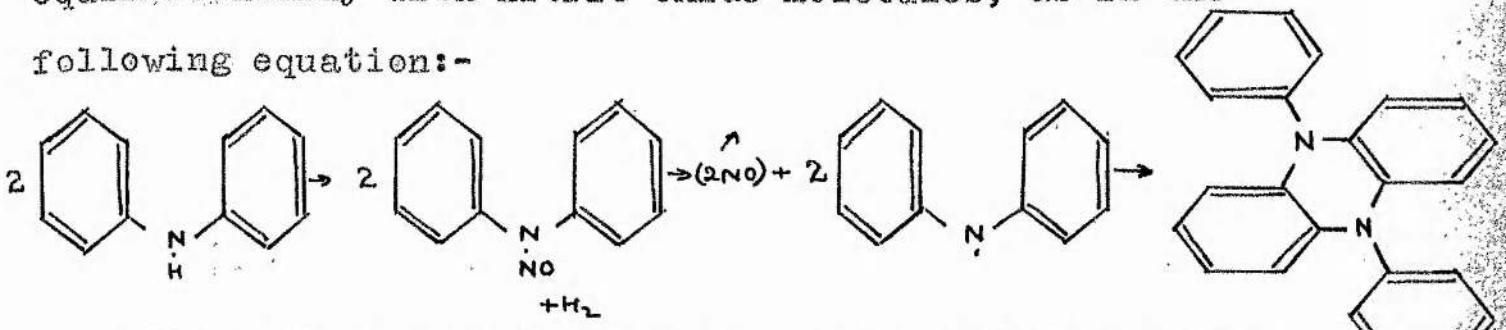
The range of conditions investigated covered times of contact from 0.199 to 1.2 seconds, partial pressures 0.1 - 1.4 mm., temperatures from 1063 to 1158°C and percentages of decomposition from 0.09 to 3.0. Towards the top of the temperature range, in the interval 1125 to 1128°C, twenty-four experiments were performed within the range of variables 0.149mm - 0.674mm. and times of contact 0.197 to 0.73 seconds. The velocity constants when calculated on a first order basis from the hydrogen production lay within the limits 0.0315 to 0.051 sec^{-1}, save for one experiment. The results obtained by varying the partial pressure of carbazole and the time of contact are shown on table 13. It seems that there is a reasonable approximation to first order behaviour to be deduced from this. The work at lower temperatures, where the percentages of decomposition were lower, show a much greater scatter in the data and it is possible that the need to achieve slight carbonisation of the reactor wall was

not adequately met at such low fractions of decomposition and this introduced a greater variability in the results. While it is not felt that a deduced energy of activation can be anything more than a first approximation the line drawn in graph XV corresponds to an equation $\log_e k = 13 - E/RT$ and yields an energy of activation of 74,400 K.cals. This value is discussed below.

Discussion.

(a) The chemical nature of the reaction.

Phenazine compounds have a six membered ring containing 2 nitrogen atoms. The formation of such a compound from diphenylamine, using the readily decomposable N.nitroso compound as starting material, is most probably a secondary reaction resulting from dimerisation of the radicals produced equimolecularly with nitric oxide molecules, as in the following equation:-

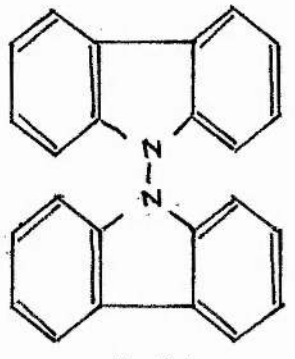


The radicals are likely to be fairly stable as they have a number of canonical structures and hence should show a considerable degree of resonance stabilisation. No tetraphenyl hydrazine is formed in contrast to the reactions of the diphenylmethyl radical, presumably because of the instability of this compound at the reaction temperature.

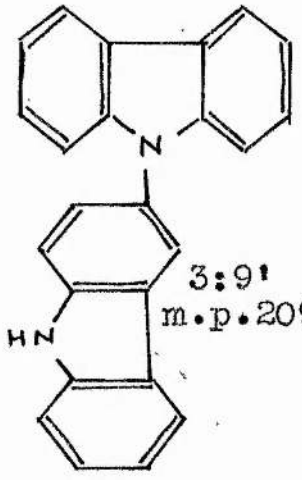
The formation of the phenazine, when first reported, led Marquerol and Florentin[105] to repeat the work and "it gave them great pleasure to confirm that....the phenazine was indeed the product", its formation being accompanied by the production of diphenylamine. This latter compound would be formed by the combination of hydrogen, liberated as a result of the phenazine formation with a Ph_2N radical.

The pyrolysis of diphenylamine by Graebe[80] yielded, among other products, carbazole. This reaction may follow a similar course to that postulated for diphenylmethane, in which diphenylmethyl radicals are formed. Subsequent formation of a link between the two phenyl rings, followed by migration of one of the eliminated hydrogen atoms to the free valency of the radical results in the formation of fluorene.

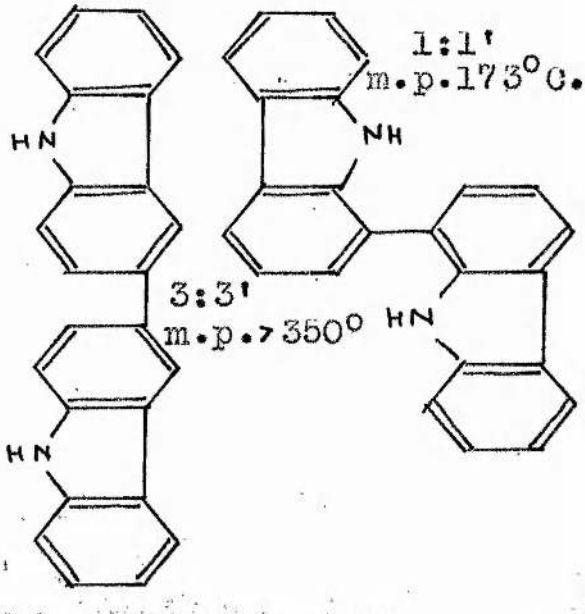
Oxidation of diphenylamine with dichromate, on the other hand, yielded diphenylbenzidine, and the work of McLintlock, Perkin and Tucker[87,88], previously noted, on the permanganate oxidation gave dicarbazyls. These compounds have the following structures:-



9:9'
m.p.221°C.



3:9'
m.p.209°C.



3:3'
m.p.>350°

1:1'
m.p.173°C.

The experimental work reported earlier proved the absence of the most probable of these compounds, 9:9' dicarbazyl, from among the pyrolytic products of carbazole. The main product was, in fact, the phenazine analogous with that obtained from diphenylamine.

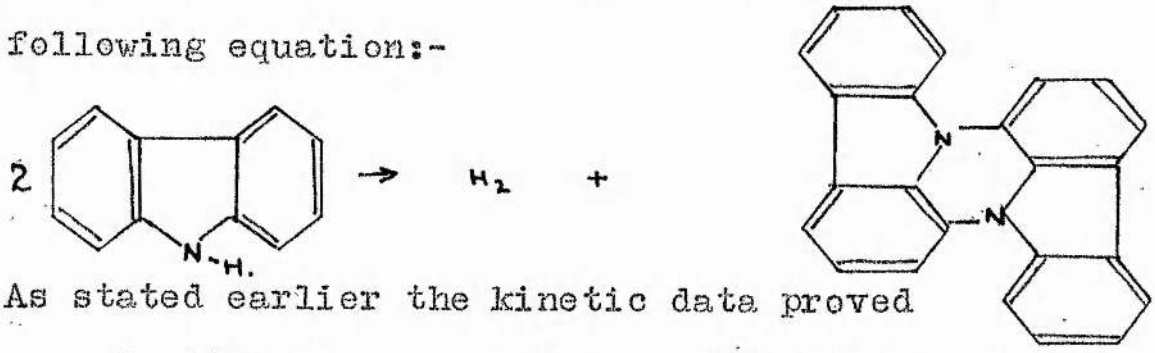
The thermal decomposition of N.nitroso diphenylamine and N.nitroso carbazole in the circulating system, using a mass spectrometer for continuous analysis, yielded hydrogen. In both experiments, some parent material, (diphenylamine or carbazole), was produced. It appears, therefore, that once hydrogen atoms are produced by the dimerisation of radicals, the union with other radicals must occur reasonably freely.

The identification of the final product was by U.V. analysis of fractions obtained during a chromatographic separation from unchanged starting material.

Examination of the spectra of homocyclic compounds and their aza- analogies shows that intensities of absorption vary, there is loss of fine structure on replacing >CH by >N; but shifts of wavelengths of maximum and minimum absorption are generally small. The absorption of aza hydrocarbons often begins at slightly longer wavelengths than that of the corresponding hydrocarbons. Whilst these rules are a useful guide in many cases, there is not much similarity between the spectra of rubicene and 1:9 - 9': 1'. carbazolylene and consequently attempted analysis of the

absorption data obtained experimentally did not yield the information desired.

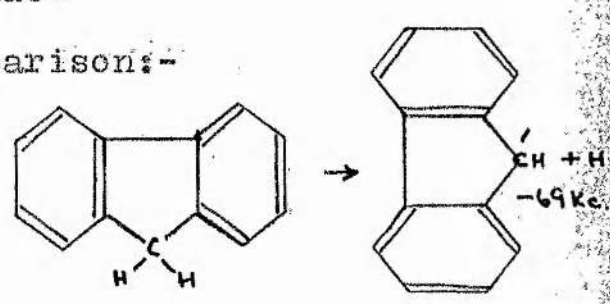
The data given earlier show that the overall reaction resulting from the pyrolysis of carbazole may be represented by the following equation:-



(b) As stated earlier the kinetic data proved troublesome in their degree of irreproducibility. Nevertheless the broad inference from graph XV is that the energy of activation is, with a rather wide margin of error, of the order of 75 K.cal. This value we ascribe to the dissociation of the N-H link in carbazole. The bond dissociation energy for NH_2-H in ammonia is 102 K.cal. This would indicate a weakening of the N-H link of the order of 27 K.cals. due to resonance energy of the free radical. There are comparatively few data with which to compare this value.

If we take the following as a comparison:-

$CH_3 - H \longrightarrow CH_3 + H - 103$ K.cals ;



there appears to be a rather greater stabilisation of the fluorenyl radical giving 34 K.cal. resonance energy. As a comparison, this is not necessarily very direct since the configurations in the carbazyl and fluorenyl radicals may be

dissimilar. In the fluorenyl radical there is probably sp^2 hybridisation of the C atom with the free valency, and the free electron conjugated with π orbitals of the ring systems. In the carbazyl radical the N.atom has three unused electrons. If two of these electrons occupy the orbital at 120° to the two bonds of the N atom in the 5 ring and the third conjugates with the π orbitals, the analogy is complete. There is no definite evidence, however, on the assignment of the 3 free electrons on the N atom and we have, therefore, to consider other points.

Free radicals involving so called "divalent nitrogen" are known to be formed by the fission of the central bond in substituted hydrazines such as $Ph_2N - NPh_2$. The precise strength of these N - N bonds is not known. The type of evidence which exists is qualitative and reminiscent of the early evidence of the dissociation of the hexa aryl ethanes. Solutions of such hydrazines have been shown to exhibit changes of colour when heated and to show deviations from Beer's Law. The colour changes have been reversible in some instances. Such behaviour in the range 0. - 100°C suggests heat of dissociation of the order of those found for hexa aryl ethanes, i.e. 8 - 11 K.cals. The heat of dissociation of the N-N bond in N_2H_4 has been determined to be 60 K.cals. Assuming a value of 10 K.cals. in the tetra aryl hydrazines, we get a weakening of the bond by 50 K.cals. equal to twice the resonance energy of the R_2N-

radical. The figure of 25 K.cal. thus arrived at is close to the 27 K.cal.deduced from carbazole pyrolysis. The agreement may be fortuitous in view of the errors in our quantities and it is certainly unfortunate that the properties of 9:9' dicarbazyl are not better known. We do not know if it shows any dissociation in solution, and it seems doubtful if it is as unstable as the tetra-aryl hydrazines since it is quoted as melting at 221°C.

The data available on matters comparable to our own work is therefore slight but it can be said to be in general agreement with the magnitude of the observed N-H bond dissociation energy in carbazole.

TOLUENE.

T O L U E N E.

The kinetics of the pyrolysis of toluene have been investigated in detail by Szwarc[31] and Steacie[40], and their work is the most relevant to the purposes of this thesis. Before dealing with the work of these authors, however, it is of interest to consider earlier work on this topic.

Tilicheev[105] found the rate of primary decomposition of toluene was thirteen times that of benzene and obtained an energy of activation of 70 K.cals/mole. Jost and Muffling[106] subjected toluene, among other compounds, to pyrolysis, following the decomposition by measurement of pressure increase. Finding that the presence of mercury dimethyl had no effect on the rate of decomposition at 690°C, they concluded that the reaction did not proceed by a chain mechanism. With these techniques, the complexity of the products prevented an investigation into the mechanism of the reaction.

By pyrolysing toluene in mercury vapour as carrier gas, Hein and Mésee[107] obtained mercury dibenzyl as a product and they were able to follow the course of the reaction by analysing for mercury. The rate depended on a number of uncontrollable factors which prevented their determining an energy of activation. Since mercury dibenzyl was formed, the first step in the reaction was postulated as:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + H \quad (i)$$

$$Hg + 2C_6H_5CH_2 \longrightarrow C_6H_5CH_2 - Hg - CH_2C_6H_5$$

The following reaction scheme, however, is equally valid to explain the production of benzyl radicals:

$$C_6H_5CH_3 \longrightarrow C_6H_5 + CH_3 \quad - \quad (ii)$$

$$C_6H_5CH_3 + CH_3 \rightarrow CH_4 + C_6H_5CH_2$$

$$C_6H_5CH_3 + C_6H_5 \rightarrow C_6H_6 + C_6H_5CH_2$$

The formation of hydrogen seems to favour scheme (i) but Hein and Mésee's use of 1000°C for the reaction temperature would cause extensive cracking of the molecule and a decision between these schemes cannot be reached from their work.

Szwarc carried out the decomposition in a form of flow system over the temperature range 738 to 864°C. The range of pressure extended from 2 to 15 mms. mercury and times of contact from 0.25 to 9 seconds. Under these conditions the percentage decomposition varied from 0.01 to 1.25, having been kept intentionally low in order to avoid secondary reactions, with the resulting complexity of products. The products were, in fact, limited to hydrogen, methane, dibenzyl, and benzene, the mechanism of their production being stated as homogeneous and first order. The energy of activation of the primary, rate determining, step was found to be 77.5 K cals/mole. The ratio of hydrogen to methane was invariably 60:40.

In the pyrolysis of o- and p-xylene somewhat similar values for the activation energy were found, 74 and 75 Kcals/mole. The experimental techniques were the same for these pyrolyses and similar decomposition mechanisms were proposed.

Szwarc proposed that the primary step in the decomposition of toluene was the initiating step in (i) above:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + \text{-}H$$

Assuming an activation energy of zero for the reverse reaction this implies that the dissociation energy of this bond is 77.5 K cals/mole. Since this is 24 K cals. less than the dissociation energy of the C-H bond in methane, we may ascribe this weakening of the toluene side chain C-H bond to the resonance energy of the benzyl radical. This is of considerable interest since the figure resulting from theoretical calculations is 13 K.cals.

The value of 77.5 K cals. for the $PhCH_2$ - H bond strength enables a heat of formation of the benzyl radical to be calculated. This value is in complete agreement with that obtained from the pyrolysis of ethylbenzene.[108]

This substance, according to Szwarc, decomposes by the primary formation of benzyl and methyl radicals and the products can be simplified by the use of toluene as carrier gas. The activation energy for the decomposition was interpreted as the dissociation energy of the $PhCH_2$ - CH_3 bond; using this experimental value and the accepted heat of formation of the methyl radical he obtained confirmation of his

previous value for the benzyl radical.

There are, however, possible reasons for questioning the experimental evidence. Szwarc's mechanism postulates that a hydrogen atom is formed first:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + \text{-H}$$

and that methane is formed as the result of the hydrogen atom attacking a toluene molecule:

$$C_6H_5CH_3 + \text{-H} \longrightarrow C_6H_5 + CH_4$$

There is not much parallel evidence for this.

The method of quantitative detection of products other than methane and hydrogen is not specified in the paper. The benzene occurring in the equations was not determined; the analysis of benzene in a large excess of toluene can only be done on a mass spectrometer, by vapour phase chromatography, or by ultra violet spectrophotometry following precision distillation. These methods are not mentioned and the evidence for the existence of benzene would appear to be stoichiometric, its presence being inferred from that of methane.

The amounts of dibenzyl were stated to approximate to the amounts of hydrogen plus methane formed. An investigation of the products of the pyrolysis of dibenzyl showed that benzyl radicals and dibenzyl, at temperatures lower than those used by Szwarc, gave toluene, benzene, and styrene. One must consider, therefore, the possibility that the benzyl radical is not as inert as is supposed by Szwarc.

Recent work by Van Artsdalen[5] on the bromination of toluene yields the value of 89.5 K.cals. for the toluene C-H bond. The kinetics of the bromination of methane[14,109] gives a value for the C-H bond in this molecule which agrees with that obtained by other techniques. The values of 89.5 and 77.5 K.cals. are difficult to reconcile and these factors tended to suggest the necessity for a re-evaluation of the toluene pyrolysis, preferably using a different technique such as the use of an inert carrier gas, and with facilities for continuous analysis. The gaseous products could thus be monitored by a mass spectrometer and the solids estimated by ultra violet absorption.

Experimental work.

The apparatus employed was identical with that used in the investigations detailed previously. Minor modifications were in the temperatures at which the traps were maintained; to allow benzene and toluene to reach the leak of the mass spectrometer, the furnace outlet trap was kept at $0^{o}C$, and, after the appropriate voltage measurements, these substances were trapped at liquid air temperature. The materials were then available for ultra violet analysis.

A distillation technique was employed to fill the container of the injector unit. Provision for a reservoir of toluene was made by blowing a side tube on the injector unit evacuating line, the reservoir being attached by cone and socket joints. With the reservoir at liquid air

temperature, the injector system was evacuated; the liquid air trap was then transferred to the injector container, and toluene distilled slowly from the reservoir.

A thermostatically controlled vessel of hot water was used to provide the necessary vapour pressure of toluene for injection to the circulating system during a run.

The toluene itself was purified by the method recommended by Szwarc. Commercially pure toluene was twice partially pyrolysed at 850°C, the product being fractionally distilled. The material was then found to give consistent pyrolytic results, Szwarc having found that unless this procedure was followed, irreproducible results were obtained due to impurities remaining after shaking with sulphuric acid, distillation and crystallisation.

Calibration of injector unit.

The container was filled by the distillation technique detailed previously. Wherever possible, standard joints were sealed with Edwards E. Wax to minimise the exposure of toluene to grease. The thermostatically controlled water bath was a metal can fitted with an immersion heater consisting of two 20 ohm ceramic resistors, supplied with power from a 50 volt transformer. The thermostat maintained the temperature to within 1C° in the 25° to 40°C working range.

The toluene delivered from the valve was estimated in

Table 14 .

Calibration of Injector Unit with Toluene.

Container Temp.	Time of Delivery.	Optical Density. 261.5	Optical Density. 268.5	Delivery of Valve. Moles/minute.
24.0°C.*	5'15"	0.767	0.708	3.13×10^{-4}.
	5'12"	0.630	0.590	
30.5°C.*	4' 4"	0.787	0.720	4.40×10^{-4}.
	4' 0"	0.710	0.652	
35.5°C.**	5' 0"	0.627	0.582	5.75×10^{-4}.
	5' 5"	0.596	0.550	

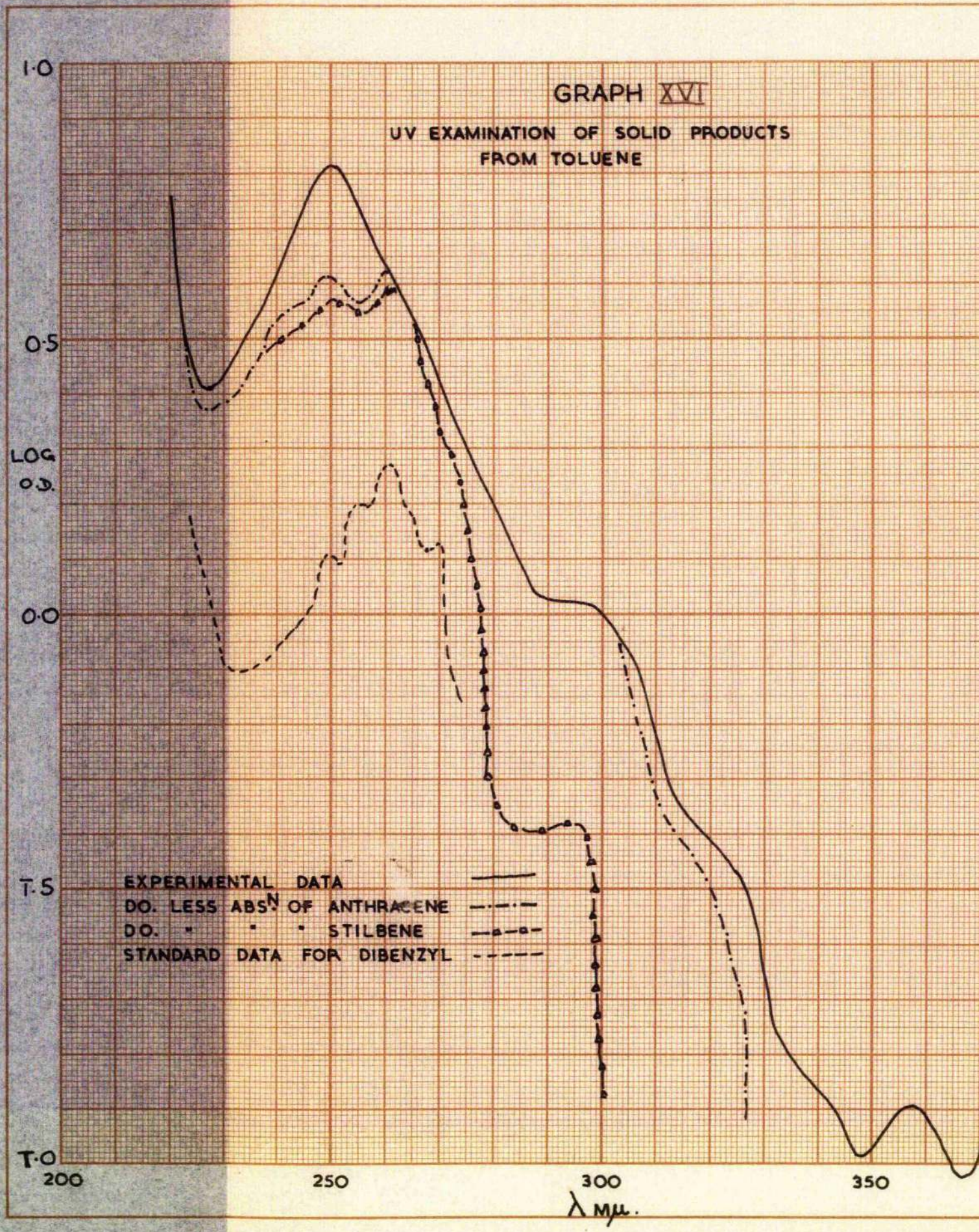
Toluene dissolved in 50mls. MeOH and diluted * 10 X.
** 20 X.

methyl alcohol solution on the U.V. spectrophotometer at 216.5 and 268.5mμ, the mean of 10 readings at each wavelength being taken. The readings were obtained by setting the wavelength control at the required value, then alternately adjusting the setting above and below this value before restoring the pointer to the exact value. Allowance was thus made for any backlash on the control. The results are tabulated opposite.

The present investigation on toluene is considered in three separate sections. Szwarc claims that dibenzyl and total gas were produced mole for mole; he calculated his reaction velocity constants on the basis that one mole of gas represented one mole of primarily decomposed toluene. Steacie, on the other hand, found the products to be dibenzyl, diphenyl, methyl and dimethyl diphenyls, and stated that the dibenzyl might account for only 50% of the solid products. A detailed discussion of his work is given in a later section but it was felt desirable to check this matter of the products under the slightly different reaction conditions used in this work.

Section 1.

Two runs were carried out at 820°C and 0.285 seconds time of contact. All the products were collected at liquid air temperature at the furnace exit, the volatile products being subsequently distilled from the solids. In one of the runs, methane was estimated during the run, and the benzene and toluene after the run. The methane amounted


GRAPH XVI
UV EXAMINATION OF SOLID PRODUCTS FROM TOLUENE
1·0
0·5
LOG O.D.
0·0
T·5
T·0
200
250
300
350
λ Mμ.
EXPERIMENTAL DATA
DO. LESS ABSN OF ANTHRACENE
DO. " " " STILBENE
STANDARD DATA FOR DIBENZYL

to 5.2×10^{-5} and the benzene to 4.25×10^{-5} moles. 3.77×10^{-3} moles toluene were undecomposed.

The solids were dissolved in 50 mls. methanol and the solution examined on the U.V. spectrophotometer.

From the location and intensity of absorption maxima dibenzyl was the major product. The maximum at 290mμ wavelength suggests the presence of styrene. Stilbene, which has a high epsilon at 320mμ was present in small concentration.

The second run was carried out under identical experimental conditions. The longer wavelength end of the spectrum was examined more critically by using solutions of higher concentration The result of the analysis, graphXVI shows the presence of anthracene. Calculation of the anthracene absorption at shorter wavelengths and deduction from the experimental result revealed the stilbene curve, along with the fine structure due to dibenzyl. The standard curve for dibenzyl is given on the graph.

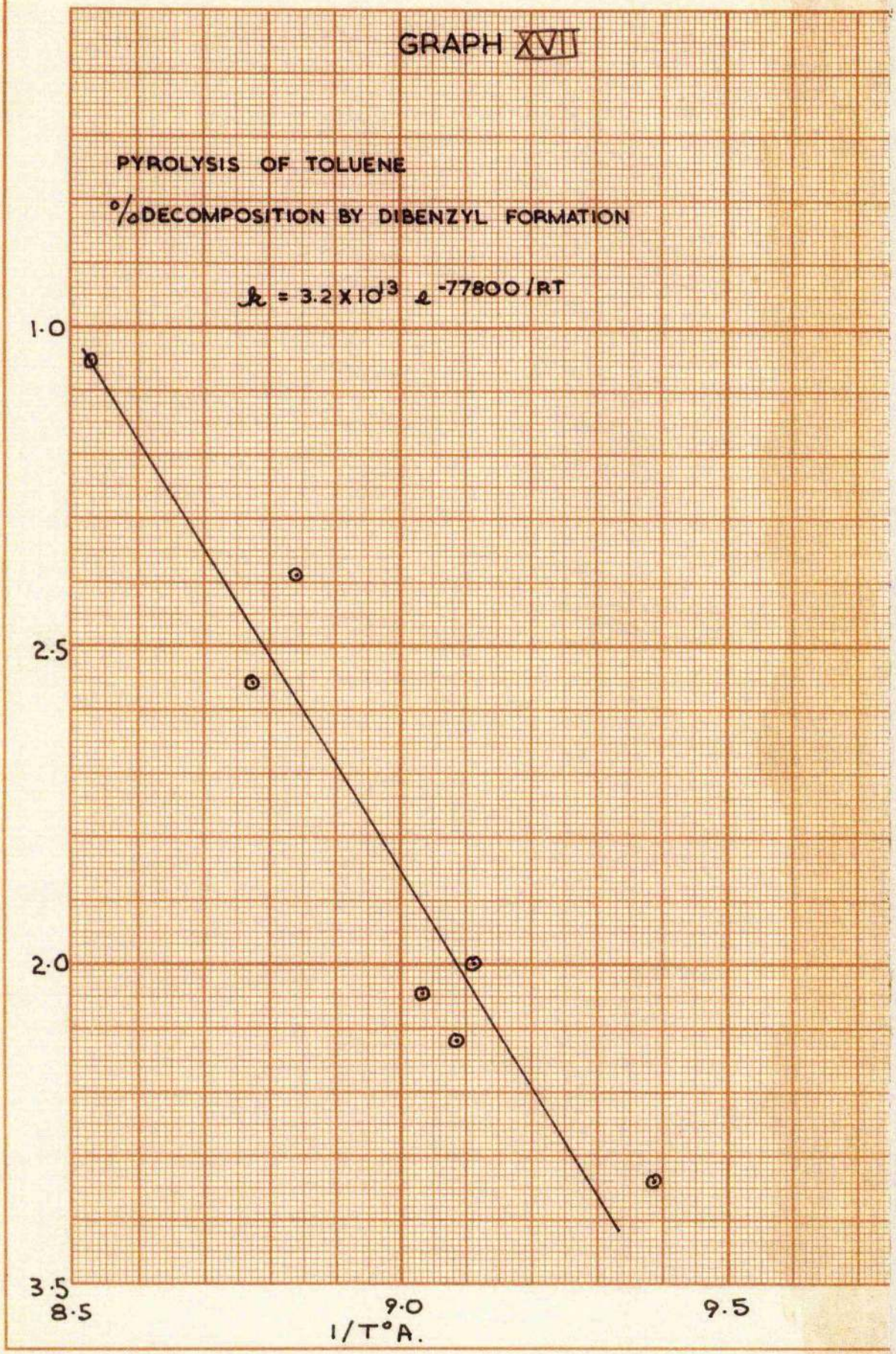
No evidence for diphenyls was obtained; these substances have $\log \epsilon \doteqdot 4$, and small amounts would have had considerable effect on the dibenzyl curve, the absorption maxima of these substances lying in the same wavelength region.

As a result of these findings it was considered that the rate of formation of dibenzyl could be used as a measure of the progress of the reaction.

Section 2.

A series of seven runs was carried out using the amount

GRAPH XVII


PYROLYSIS OF TOLUENE
% DECOMPOSITION BY DIBENZYL FORMATION
$k = 3.2 \times 10^{3} e^{-77800/RT}$
1·0
2·5
2·0
3·5
8·5
9·0
9·5
1/T°A.

of dibenzyl produced as an indication of the decomposition; the estimation was carried out on the U.V. spectrophotometer. The dibenzyl was collected in the furnace outlet trap at 0°C under conditions which allowed toluene and benzene to remain in the vapour phase. On completion of each run a solution of the product in methanol was examined. On graphXVI it is seen that the absorption of dibenzyl decreases sharply from 270 - 275mμ, whereas that of stilbene, if present, continues beyond this value. The method of analysis, therefore, was to measure the optical density due to stilbene at 290mμ, calculate its density at 257mμ, deduct this value from the observed value, and hence calculate the concentration of dibenzyl.

Pure dibenzyl was obtained by chromatographic separation of the bulked products and identified by melting point. No diphenyl was detected during this separation. Optical evidence indicated that stillbene was present in exceedingly small amount, but it was not possible to get sufficient material for a melting point determination. The concentration of this material was of the order of 10^{-3} times that of the dibenzyl.

Velocity constants were calculated from the expression:

$\log k = 2.303/t \cdot \log 100/100 - \%$ decomposition, where

t = time of contact.

It was not intended to make a exhaustive check of the dependence of log k against 1/T°k by these analyses for dibenzyl but it can be seen from graphXVII that a linear relationship represented by:

$$\log_{10} k = 13.5 - \frac{77,800}{4.57T}$$

does not conflict with the observations.

These data are therefore in reasonable agreement with the results of Szwarc based on the gaseous products of the reaction.

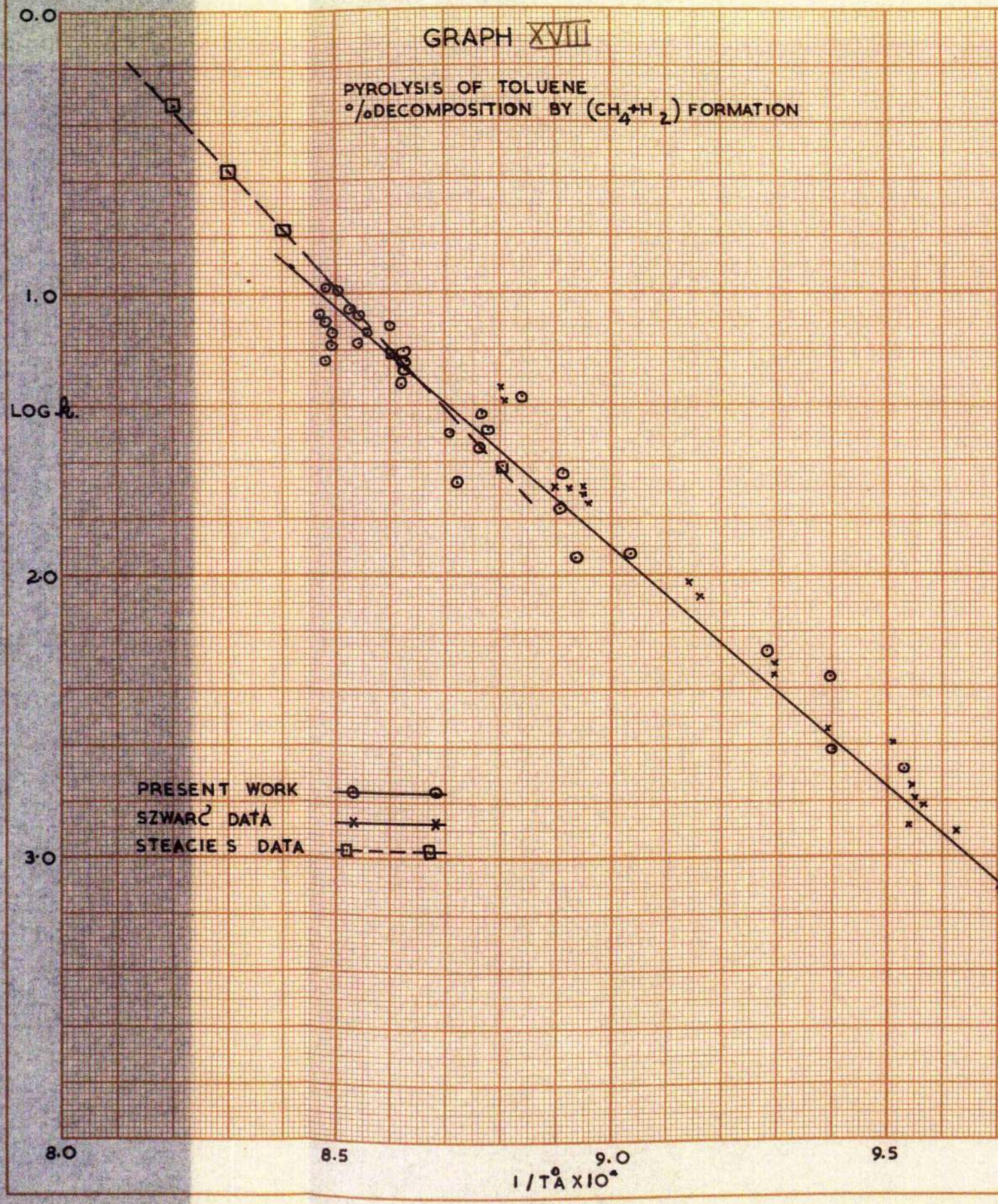
Section 3.

The third part of the present work was a repetition of the above series using the amount of gas formed to measure the toluene decomposition.

The mass spectrometer was used for the analyses and a prerequisite of the work was a simple means of constantly checking the sensitivity of the instrument with respect to hydrogen and methane.

A 5 litre bulb filled with pure methane was attached to the apparatus near the gas burette. By means of a system of taps either hydrogen (from a cylinder) or methane could be introduced into the burette and the amount measured.

Known amounts of each gas were transferred in turn from the burette to a short limb of the apparatus and there mixed. The mixture was then drawn back into the burette; there was thus a known number of moles of gas, the molar ratio of the constituents being known, within the burette at the start of each run. It was possible between individual runs to inject small known amounts of the mixture into the circulating system and measure increases in the recorded voltages of the two gases, thus allowing accurately for changes in sensitivity. The results showed that, in actual fact, the sensitivity remained satisfactorily constant.


GRAPH XVIII
PYROLYSIS OF TOLUENE
% DECOMPOSITION BY (CH_4+H_2) FORMATION
0.0
1.0
2.0
3.0
LOG k.
PRESENT WORK
SZWARC DATA
STEACIE S DATA
8.0
8.5
9.0
9.5
1/TA X 10⁴

A further refinement in technique was provision of a means for accurately measuring the toluene delivered from the injector during each set of runs. One limb of a small Quickfit tap was sealed and blown into a bulb of about 2 mls. capacity, the other limb being fixed to a B10 cone. This container was attached to a B10 socket blown in the side of the furnace exit trap, which was maintained at liquid air temperature until completion of the set of runs when, by transference of the liquid air Dewar from the trap to the container bulb, distillation of the toluene and benzene took place. The container was removed and weighed at room temperature.

That methane and hydrogen were the only two gaseous products was confirmed by a qualitative scan on the mass spectrometer.

Considerably more methane was formed during these runs than had been obtained by Szwarc, who invariably found the ratio of hydrogen to methane to be 60:40. This feature will be discussed later.

Calculations of the results on the basis of a first order decomposition mechanism gave values for the energy of activation and non exponential factor in agreement with those obtained previously. On graph XVIII a full set of results is given for both sections of the present work. The results of the work of Szwarc are also shown.

Discussion.

Two values of the energy of activation of the primary decomposition of toluene have been quoted, 89.5 and 77.5 K.cals/mole. In the brief investigation described, agreement with the latter figure is excellent. The non exponential term is in agreement with the accepted conception of first order behaviour as suggested theoretically by Polanyi and Wigner.[110]

While the work of this thesis was being done, Steacie published results on the pyrolysis of toluene under somewhat different conditions to those of Szwarc. Szwarc confined his experiments to the temperature range 738°C to 864°C, and worked at partial pressures of toluene from 2.7 to 13.7 mms. mercury. Steacie's lower limit of temperature was 856°C extending to 946°C; the range of partial pressures extended from 1.05 to 2.36 cms. The work of Szwarc has been described in the introductory paragraphs of this section and an examination of Steacie's data is now relevant.

Several points in connection with the work require discussion. The experimental method, in principle, was identical with that of Szwarc in that toluene, introduced from a containing vessel to a reactor, was then passed to cold traps; the volatile products were continuously removed by means of a diffusion pump. The kinetic data were obtained in a reaction vessel 24 cms. long and 54.5 mls. volume.

The investigation into the relation between reaction velocity and time of contact yielded data which, when expressed graphically, gave a curve showing constant first order rate constant at times of contact in excess of 0.5 seconds, using a partial pressure of toluene of 1.2 cms. Hg. When the partial pressure was increased to 2 cms., this "limiting" contact time was reduced to 0.35 seconds. Despite this finding, the data upon which the energy of activation is based were obtained with a constant contact time of 0.068 seconds.

Steacie concluded that the decomposition could not be considered as being first order, and, if it was assumed to be so, then the energy of activation became 90 K.cals.

When we compare the results of Szwarc and Steacie et al. we observe the following differences about the products:

(a) The gaseous products, hydrogen and methane, are in the ratio 1.5/1 according to Szwarc and 2/1 according to Steacie.

(b) Steacie showed that the C_6H_6/CH_4 ratio was approximately 1/1 whereas Szwarc assumed this to be the case.

(c) Szwarc considers dibenzyl to be the sole solid product while Steacie views it as being about 50% of the total and the rest being dimethyl diphenyls.

The work of Steacie et al. is clearly of greater detail on this matter but it suffers from one surprising defect. The primary aim of their work was to repeat the conditions used by Szwarc but in practice they used higher temperatures. The actual temperature used for the experiments on the nature of

the products is not given in Steacie's paper but the range quoted in other parts of the paper is 1120°K to 1220°K. The highest temperature used by Szwarc was 1137°K and his kinetic data were taken down to 1011°K. It is evident that there was little overlap in the reaction conditions and those used by Steacie were more vigorous. This would be expected to produce a greater variety of products and in view of this unfortunate discrepancy it cannot be considered that Steacie's work is a definite refutation of Szwarc's claims.

The time available for this work did not permit an exhaustive check of these discrepancies to be made. The temperature range investigated, 1030°K to 1179°K, approaches the lower limit used by Szwarc and extends into the range used by Steacie. The graph giving the U.V. examination of products shows the prominence of the features shown by dibenzyl - a substance which is a weak absorber and easily masked by traces of other compounds such as diphenyls and stilbene which have extinction coefficients greater by 100. Using the methods of analysis detailed earlier the total moles of hydrogen plus methane in expts. 3 and 5 were 0.48 and 0.72 whereas 0.52 and 0.75 moles of dibenzyl were foundrespectively. Thus the basic scheme of Szwarc seems to explain the reaction products in the lower temperature range.

Primary reaction $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$ (1)

Secondary reactions of H atoms.

$H + C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H_2$ (2)

$H + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3$ (3)

$CH_3 + C_6H_5CH_3 \rightarrow C_6H_5CH_2 + CH_4$ (4)

$2\ C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5$ (5)

The present work used partial pressures of toluene which were more than 10-fold less than those used by Steacie and Szwarc and an inert carrier gas. This difference appears to affect the H_2/CH_4 ratio considerably. The hydrogen no longer exceeds the methane by a factor of 1.5 to 2 but is less than it with the H_2/CH_4 ratio varying from about 0.25 to 0.75. This feature requires more detailed confirmation as it is difficult to explain on the basis of equations (2) and (3) where the relative frequency of the processes would not vary with toluene concentration. If the production of H_2 occurred mainly by

$$H + H + C_6H_5CH_3 \longrightarrow H_2 + C_6H_5CH_3 \qquad (6)$$

rather than by process (2), then a reason would exist for this behaviour. It may be significant in this connection that Steacie's average pressures of toluene were somewhat higher than those used by Szwarc and this was accompanied by a higher proportion of hydrogen in the gaseous products. On the other hand in the present work the nitrogen carrier gas was available at a pressure of 5-6 mms. and would have been expected to show some efficiency as a third body. If this last suggestion (6) proved correct the inefficiency of the nitrogen is very surprising.

With regard to the other products the present work provides

no detailed evidence. Rates of reaction based on dibenzyl estimations appear to give a temperature dependence in agreement with Szwarc's data based on (H_2 CH_4) production (GraphXVII) and with the similar data of the present work (Graph XVIII).

Turning to the quantitative data on the pyrolysis of toluene Steacie et al. assert that calculated first order constants increase by 90% with an 800% increase in time of contact, increase by 10% for a 65% increase in pressure of reactant and increase somewhat for an unspecified change in the ratio of surface to volume of the reaction vessel. Szwarc detected no appreciable effect of any of these parameters, but his data were not extensive. The present work does not provide sufficient data to amplify this position and first order constants have been used for contact times of 0.3 to 0.8 seconds and partial pressure of 0.5 to 1.8 mm. toluene.

In surveying the values of activation energy to be deduced the preliminary conclusions of the work given here would be to agree with Szwarc's value of E = 77.8 as representing the temperature coefficient of the reaction. Steacie's conclusion that calculated first order constants have a temperature coefficient requiring 90 K.cals. for the energy of activation is based on velocity constants from experiments with contact times of 0.068 seconds. At high temperatures of 1200°K. and pressures of gas of 20mms. it seems unlikely that heat conduction can bring all the gas up to these temperatures in this short time and this might account for the variations of $\underline{k}$ observed with change of contact

time. If the data of Steacie are plotted on the same graph as the data of this work and those due to Szwarc, we have a coverage on this reaction which extends from 1011°K to 1220°K. This is a very large range of temperature and a value of E of about 78 K. cals.clearly represents the temperature variation better than one of 90. Moreover the temperature independent factor is 2.4×10^{13} with this lower value of E, while for E = 90 the non-exponential term can be calculated to be $10^{15.7}$. Steacie did not evaluate this term and so made no comment on its unusual magnitude for a unimolecular process.

The conclusion can be drawn from this work that the pyrolysis of toluene can be followed by estimations of dibenzyl, or hydrogen and methane, and, while considerable uncertainties in the mechanism remain to be resolved, the temperature coefficient of the process is governed by an activation energy of 77-78K.cals. This would be in agreement with the value due to Szwarc.

Experimental Results.

1. Triphenyl Methane.

Run No.	T°K.	Time of run. mins,	p_{N_2} mms.	t. secs.	TPM$_4$ x10 moles.	H_2 x10^5	pp TPM mms.	%dec	k.
26	994	3.13	5.4	.418	2.64	.52	.120	1.97	.0471
27	994	3.68	5.4	.421	3.15	.64	.123	2.03	.0482
11	995	6.03	4.52	.295	5.14	.51	.086	.99	.0360
12	996	7.55	4.67	.342	6.43	.70	.124	1.09	.0318
17	996	5.0	5.18	.469	4.26	.12	.136	2.82	.0609
67	996	3.90	5.2	.416	9.64	1.14	.372	1.18	.0288
105	996	3.05	5.2	.502	2.31	.22	.130	0.95	.0189
106	996	3.00	5.2	.481	2.28	.33	.126	1.44	.0301
107	996	3.03	5.2	.488	2.30	.26	.126	1.13	.0231
108	996	3.05	5.2	.486	2.31	.35	.125	1.51	.0312
109	996	3.05	5.2	.488	2.31	.35	.126	1.51	.0312
110	996	3.0	4.62	.639	2.28	.57	.164	2.50	.0391
111	996	3.0	4.63	.657	2.28	.48	.168	2.10	.0320
112	996	3.01	4.70	.643	2.287	.48	.164	2.10	.0326
113	996	3.0	6.82	.702	2.28	.48	.182	2.10	.0299
114	997	3.0	6.9	.734	2.28	.67	.19	2.94	.0395
115	997	3.0	6.9	.712	2.28	.59	.185	2.6	.0369
68	998	3.73	5.2	.414	9.2	1.88	.335	2.04	.0495
32	1001	2.15	5.1	.385	1.83	.32	.112	1.75	.0458
116	1003	3.03	4.68	.50	2.27	.54	.128	2.38	.0474
117	1003	3.13	4.68	.505	2.34	.60	.129	2.56	.0514
118	1003	3.06	4.70	.498	2.29	.45	.182	1.96	.0400
119	1003	3.0	4.02	.865	2.246	.64	.216	2.86	.0389
120	1003	3.06	4.16	.973	2.291	.97	.240	4.23	.0442
121	1003	3.05	4.17	.931	2.28	.91	.232	4.0	.0438
123	1003	3.0	5.43	.925	2.24	.97	.234	4.33	.0479
124	1003	3.01	5.41	.822	2.25	.87	.208	3.86	.0479
125	1003	3.0	5.42	.760	2.246	.67	.193	2.98	.0398
128	1003	3.05	5.85	.278	2.28	.37	.072	1.62	.0587
129	1003	3.01	5.80	.285	2.253	.355	.074	1.58	.0553
138	1003	2.23	4.30	.734	3.75	.47	.395	1.25	.0169
139	1003	2.28	4.30	.732	3.869	1.45	.396	3.75	.0521
143	1003	2.25	4.80	.285	3.818	.56	.165	1.46	.0515
158	1003	2.78	4.30	.544	2.226	.26	.183	1.15	.0215
159	1003	2.68	4.30	.542	2.146	.39	.183	1.82	.0333
160	1003	3.72	4.32	.212	3.466	.29	.182	0.83	.0400
13	1004	4.0	5.07	.478	3.40	.91	.139	2.68	.0568
14	1004	4.0	4.60	.599	3.40	1.22	.173	3.59	.0610
122	1004	3.03	4.20	.929	2.268	.81	.232	3.57	.0392
126	1004	3.08	5.50	.807	2.306	1.04	.204	4.51	.0570
127	1004	3.10	5.82	.279	2.253	.23	.073	1.02	.0366
130	1004	2.00	4.80	.492	3.394	.88	.278	2.60	.0534
134	1004	2.13	4.20	.777	3.614	1.12	.419	3.10	.0392
135	1004	2.20	4.21	.763	3.733	1.04	.412	2.79	.0371

Run No.	T°K.	Time of run. mins.	p_{N_2} mms.	t. secs.	TPM $\times 10^4$ moles	H_2 $\times 10^5$	pp TPM mms.	%dec.	k.
8	948	8.0	4.55	.320	6.81	.128	.09	.188	.0057
88	950	3.43	5.12	.180	4.25	.050	.18	.12	.0063
83	951	3.0	5.20	.489	6.33	.12	.32	.19	.0039
89	951	9.0	4.65	.382	7.66	.17	.10	.22	.0058
79	953	3.16	5.20	.488	6.66	.25	.32	.37	.0077
84	953	3.0	5.18	.483	6.33	.12	.32	.19	.0039
85	953	3.0	4.63	.302	6.33	.14	.20	.22	.0073
86	953	3.0	4.65	.313	6.33	.10	.21	.16	.0051
89	953	3.71	5.12	.453	4.60	.09	.18	.20	.0043
90	955	3.25	5.12	.453	4.03	.032	.18	.08	.0017
103	955	5.0	5.15	.462	6.20	.13	.185	.21	.0045
104	955	6.03	5.12	.461	7.47	.32	.185	.43	.0093
80	956	3.06	5.20	.483	6.45	.16	.32	.24	.0051
91	957	3.46	5.12	.453	4.29	.12	.183	.28	.0061
81	958	3.01	4.65	.304	6.35	.14	.207	.22	.0072
102	958	3.41	5.18	.451	4.23	.22	.182	.52	.0115
92	959	3.65	5.12	.450	4.52	.17	.182	.38	.0083
82	960	3.00	4.65	.306	6.33	.10	.208	.16	.0052
18	963	7.0	5.15	.482	5.96	.29	.68	.49	.0101
101	963	5.0	5.20	.439	6.20	.24	.184	.39	.0088
94	966	4.0	5.12	.447	4.96	.32	.181	.64	.0144
98	967	4.0	5.20	.439	4.96	.21	.179	.42	.0100
99	967	4.13	5.20	.439	5.12	.26	.178	.50	.0115
100	967	4.00	5.20	.439	4.96	.29	.178	.58	.0130
95	969	4.00	5.12	.445	4.96	.32	.181	.64	.0145
97	969	4.0	5.15	.441	4.96	.35	.180	.70	.0162
96	972	4.0	5.18	.447	4.96	.21	.183	.42	.0098
19	973	5.05	5.42	.423	4.30	.51	.071	1.19	.0281
20	976	4.73	5.40	.424	4.03	.42	.075	1.04	.0244
21	979	3.06	5.4	.418	2.61	.32	.075	1.23	.0297
22	984	3.08	5.41	.418	2.62	.35	.075	1.33	.0318
29	984	4.0	5.4	.427	3.40	.44	.152	1.29	.0308
31	984	5.0	5.4	.428	4.26	.44	.123	1.03	.0241
64	985	3.71	5.2	.419	9.16	.50	.335	.54	.0132
23	986	3.71	5.42	.415	3.15	.36	.075	1.14	.0275
30	986	3.75	5.4	.426	3.19	.38	.122	1.19	.0282
6	988	12.2	5.67	.321	16.46	1.30	.204	.80	.0246
65	990	3.61	5.18	.420	8.91	.60	.336	.67	.0160
24	991	4.05	4.8	.230	3.45	.24	.042	.69	.0302
10	993	5.06	5.0	.485	4.29	.87	.139	1.13	.0232
16	993	4.0	5.2	.463	3.40	.96	.134	2.82	.0609
25	993	3.63	5.0	.290	3.07	.29	.053	.94	.0326
28	993	3.60	5.4	.423	3.06	.67	.122	2.19	.0517
66	993	3.35	5.2	.416	8.27	.68	.335	.83	.0199

Run No.	T°K.	Time of Run. mins.	p_{N_2} mms.	t. secs	TPM $\times 10^4$ moles.	H_2 $\times 10^5$ moles.	pp TPM. mms.	%dec.	k.
136	1004	2.10	4.21	.743	3.563	1.15	.402	3.23	.0442
137	1004	2.16	4.20	.740	3.665	1.34	.401	3.65	.0503
140	1004	2.30	4.80	.288	3.903	0.59	.167	1.51	.0525
141	1004	2.60	4.80	.287	4.412	.37	.166	.84	.0292
142	1004	2.18	4.80	.284	3.70	.59	.164	1.60	.0562
157	1004	2.12	4.25	.529	2.12	.43	.178	2.02	.0387
71	1005	3.36	4.40	.280	8.30	1.27	.231	1.53	.0546
72	1005	2.55	4.70	.322	6.30	1.30	.265	2.06	.0641
73	1005	2.50	4.70	.338	6.175	1.40	.277	2.27	.0671
74	1005	2.50	5.1	.458	6.175	1.15	.372	1.86	.0407
75	1005	3.50	5.3	.465	8.80	2.50	.518	2.86	.0619
131	1005	2.03	4.85	.467	3.44	1.07	.264	3.10	.0677
132	1005	2.0	4.94	.447	3.394	.58	.255	1.71	.0382
133	1005	1.50	5.0	.437	2.554	.45	.193	1.76	.0403
161	1005	1.0	4.0	.407	.79	.17	.136	2.15	.0529
164	1005	1.15	4.0	.410	.92	.21	.138	2.28	.0557
165	1005	1.58	4.0	.408	1.26	.247	.139	1.96	.0480
76	1006	2.50	5.32	.423	6.17	.88	.346	1.42	.0338
162	1006	3.06	3.95	.397	2.45	.38	.136	1.57	.0394
163	1006	3.94	3.95	.404	1.53	.32	.125	2.10	.0518
154	1007	2.55	4.20	.551	2.04	.71	.187	3.48	.0644
155	1007	2.35	4.20	.551	1.88	.72	.185	3.83	.0708
156	1008	2.50	4.22	.549	2.00	.80	.185	4.00	.0744
33	1010	2.68	5.15	.433	2.30	.81	.128	3.52	.0828
15	1011	4.0	5.10	.461	3.405	1.33	.135	3.91	.0863
34	1011	3.0	5.15	.428	2.55	0.93	.126	3.65	.0869
5	1024	12.0	6.0	.403	20.42	5.56	.228	2.72	.0685
35	1025	3.8	5.20	.429	3.23	1.50	.185	4.62	.1108
37	1031	3.74	5.30	.420	3.18	1.9	.194	5.97	.1466
38	1031	6.58	5.35	.415	5.58	.16	.335	2.86	.0701
39	1031	3.44	5.47	.412	2.92	.175	.159	6.0	.1501
36	1033	2.68	5.25	.425	2.30	.151	.129	6.57	.1605
41	1038	2.51	5.0	.214	2.14	.50	.065	2.33	.1092
42	1040	2.53	5.2	.266	1.34	.62	.081	4.63	.1781
43	1041	2.68	5.6	.40	2.27	1.67	.121	7.35	.1910
44	1042	2.71	5.65	.396	2.31	1.66	.121	7.18	.1883
63	1045	2.76	5.70	.397	2.35	1.36	.121	5.79	.1501
45	1048	2.76	5.74	.389	2.35	1.30	.119	5.53	.1464
46	1049	2.43	5.80	.386	2.07	1.58	.118	7.66	.2065
47	1049	2.50	5.20	.211	2.13	1.30	.066	6.10	.2985
62	1049	2.66	5.65	.394	2.265	1.69	.121	7.46	.1968
166	1049	2.0	4.45	.519	1.60	1.65	.183	10.31	.2098
167	1051	2.06	4.52	.513	1.65	1.74	.182	10.54	.2173
168	1052	2.20	4.52	.527	1.65	2.12	.186	12.50	.2609

Run No.	$T^{\circ}K.$	Time of Run. mins.	p_{N_2} mms.	t. secs.	TPM $\times 10^4$ moles.	H_2 $\times 10^5$ moles.	pp TPM mms.	%dec.	k.
61	1052	2.20	5.60	0.393	1.16	1.46	0.121	12.52	0.3404
150	1055	2.43	5.40	0.450	4.14	4.07	0.160	9.84	0.2335
169	1055	2.06	4.62	0.517	1.54	1.76	0.184	11.42	0.2349
170	1056	2.20	4.70	0.510	2.06	0.97	0.169	4.71	0.0946
171	1056	2.03	4.68	0.501	1.52	1.65	0.179	10.85	0.2294
50	1057	2.60	5.42	0.262	2.21	1.27	0.081	5.75	0.2270
172	1059	2.13	4.80	0.495	1.59	1.17	0.177	7.35	0.1544
51	1063	2.41	4.70	0.222	2.05	2.15	0.069	10.48	0.4992
52	1063	2.43	4.80	0.216	2.07	1.83	0.067	8.84	0.4287
53	1063	2.48	4.90	0.211	2.11	1.59	0.066	7.53	0.3714
60	1063	2.30	4.45	0.399	2.80	2.84	0.124	10.14	0.2679
59	1067	2.63	5.40	0.400	2.24	3.12	0.124	13.95	0.3750
54	1068	2.66	5.55	0.386	2.27	3.32	0.120	14.62	0.4090
58	1068	2.35	5.20	0.409	2.00	3.98	0.127	19.90	0.5270
55	1070	2.73	5.65	0.385	2.32	2.97	0.120	12.80	0.3558
56	1071	3.25	5.80	0.363	2.76	3.71	0.120	13.46	0.3980
57	1071	3.05	5.90	0.375	2.59	3.42	0.117	13.20	0.3752

Experimental Results.

2. Carbazole.

Run	Temp. °K.	Time of run. mins.	Moles Carbazol x10^4	Time of Contact secs.	Partial pressure Carbazol mm.	Moles H_2x10^5	% dec	k sec^{-1}
82	1063	4	5.6	.655	.326	.172	.307	.0049
44	1065	10	14.0	.487	.257	.317	.226	.0046
75	1067	2.86	4.00	.535	.267	.282	.705	.0132
104	1068	2.95	5.39	.697	.410	.41	.760	.0109
105	1068	3.00	5.49	.696	.407	.145	.264	.0039
103	1069	2.9	5.30	.698	.463	.130	.245	.0036
76	1070	2.83	3.96	.554	.280	.182	.460	.0083
78	1070	2.51	3.51	.680	.294	.177	.504	.0074
79	1070	2.63	3.68	.683	.359	.112	.305	.0047
80	1070	2.78	3.89	.693	.359	.204	.524	.0076
101	1070	2.75	5.03	.550	.346	.07	.139	.0025
77	1071	2.83	3.96	.536	.271	.182	.460	.0086
100	1071	3.0	5.49	.548	.350	.10	.191	.0037
102	1071	2.9	5.30	.549	.353	.18	.349	.0062
42	1072	9.33	13.06	.493	.245	.253	.197	.0042
68	1072	2.41	3.37	.858	.235	.150	.446	.0051
43	1073	9	12.60	.483	.234	.725	.575	.0119
32	1073	5	9.25	.431	.291	.563	.614	.0144
62	1073	3.41	4.77	.596	.295	.204	.427	.0073
31	1075	5	9.25	.449	.295	.583	.630	.0143
41	1075	8.13	11.38	,498	.243	.478	.42	.0083
63	1076	3.01	4.21	.583	.295	.322	.76	.0131
74	1076	4.0	5.6	.604	.300	.231	.412	.0068
99	1076	2.83	5.17	.576	.362	.045	.087	.0016
33	1077	15	21.0	.723	.354	1.605	.764	.0108
40	1078	7.15	10.01	.498	.253	.65	.649	.0134
98	1078	2.7	4.94	.567	.374	.235	.475	.0085
93	1080	2.63	4.81	.563	.366	.236	.491	.0089
73	1081	2.91	4.07	.608	.325	.225	.55	.0091
90	1081	2.86	5.23	.567	.364	.209	.400	.0073
92	1081	3.11	5.69	.552	.362	.166	.292	.0054
97	1081	2.70	4.94	.559	.374	.180	.364	.0065
39	1082	7	9.80	.497	.256	.735	.75	.0152
91	1082	2.90	5.30	.552	.362	.166	.314	.0057
72	1083	2.5	3.50	.790	.384	.107	.307	.0038
61	1085	3.0	4.2	.581	.275	.387	.921	.0158
71	1085	3.0	4.2	.752	.380	.193	.460	.0061
29	1088	5.0	9.25	.441	.293	.523	.565	.0128
30	1089	5	9.25	.443	.290	.373	.403	.0091
70	1090	2.16	3.02	.796	.382	.317	1.045	.0132
67	1090	4.05	5.67	.786	.385	.182	.321	.0041
96	1090	2.53	4.63	.588	.382	.107	.232	.0039
34	1091	10.0	14.0	.618	.307	1.28	.91	.0148
35	1091	5	7.00	.631	.318	.498	.712	.0112
88	1092	2.71	4.96	.566	.372	.236	.427	.0076

Run	Temp °k.	Time of run. mins.	Moles Carbazol $x10^4$	Time of contact. secs.	Partial pressure Carbazol. mm.	Moles $H_2 x10^5$	% dec.	k.
89	1092	2.78	5.08	.550	.357	.225	.443	.0080
60	1093	3	4.2	.577	.290	.403	.95	.0166
87	1093	2.8	5.12	.554	.354	.209	.409	.0074
95	1093	2.56	4.68	.541	.350	.188	.401	.0074
94	1094	2.45	4.48	.54	.352	.215	.479	.0085
59	1099	3.08	4.31	.578	.297	.44	1.022	.017
65	1101	2.16	3.02	.845	.413	1.51	3.17	.038
57	1104	3	4.2	.614	.302	.92	2.19	.036
58	1104	3	4.2	.580	.300	.50	1.20	.020
56	1105	3	4.2	.599	.297	.94	2.25	.038
64	1105	2.48	3.47	.792	.390	1.015	2.92	.037
55	1105	3	4.20	.552	.274	.849	2.02	.0371
54	1109	3.03	4.21	.406	.212	.473	1.116	.027
154	1110	2.06	1.112	.425	.108	.094	.845	.0200
125	1111	2.01	7.47	.286	.350	0.258	0.349	.0121
124	1112	2.03	7.47	.306	.353	0.277	0.375	.0128
53	1112	3.08	4.31	.401	.211	.317	.735	.0184
52	1114	3	4.2	.406	.214	.268	.639	.0155
123	1114	2.03	7.47	.310	.99	.370	.490	.0159
156	1115	2.0	1.08	.520	.107	.016	1.4	.0288
119	1117	2.03	7.47	.626	.723	1.106	1.48	.0236
116	1118	2.0	7.36	.726	.845	.585	.795	.0107
51	1119	2.0	2.8	.397	.211	.541	1.98	.0503
117	1119	2.08	7.65	.663	.775	1.014	1.325	.0201
118	1119	2.08	7.65	.625	.726	.798	1.04	.0167
128	1119	2.0	7.36	.264	.306	.245	.332	.0126
126	1120	2.01	7.39	.250	.292	.426	.577	.0231
127	1120	2.01	7.39	.265	.292	.356	.482	.0183
120	1121	2.05	7.54	1.22	1.42	1.436	1.90	.0156
121	1121	2.0	7.36	1.11	1.31	1.585	2.15	.0197
122	1121	2.06	7.58	1.11	1.30	1.722	2.27	.0205
50	1122	2.0	2.8	.557	.294	.521	1.86	.0336
49	1124	2.0	2.8	.551	.307	0.59	2.12	.0382
112	1124	2.0	7.36	.267	.347	0.415	0.564	.0211
143	1124	2.0	7.36	.196	.448	.588	.80	.0407
168	1124	2.91	1.629	.853	.178	.026	1.60	.0187
140	1125	2.0	7.36	.199	.481	.519	.705	.0354
165	1125	2.93	1.58	.731	.149	.042	.260	.0365
141	1125	2.2	8.09	.201	.457	.670	.828	.0412
132	1126	2.01	3.61	.208	.231	.327	0.905	.0435
133	1126	2.06	3.70	.208	.230	.345	0.934	.0450
134	1126	2.00	3.60	.206	.230	.378	1.05	.0514

Run	Temp. °K.	Time of run. mins.	Moles Carbazol $x10^4$	Time of Contact secs.	Partial pressure Carbazol. mm.	Moles $H_2 x10^5$	% dec.	k.
135	1126	2.0	3.60	.204	.229	.343	.95	.0474
136	1126	2.08	3.74	.205	.229	.364	.97	.0475
137	1126	2.01	3.61	.203	.225	.700	1.94	.0964
138	1126	2.01	3.61	.205	.227	.357	.99	.0485
139	1126	2.21	3.97	.201	.211	.355	.894	.0447
142	1126	2.20	8.09	.197	.451	.500	.618	.0314
144	1126	2.11	3.16	.199	.159	.277	.875	.0442
145	1126	2.13	3.19	.215	.173	.325	1.02	.0476
146	1126	2.11	3.16	.211	.169	.278	.88	.0419
48	1127	3.0	4.20	.583	.286	0.86	2.04	.0355
106	1127	2.10	7.73	.554	.674	1.45	1.876	.0336
107	1127	2.00	7.36	.440	.567	1.096	1.489	.0334
108	1127	2.04	7.51	.423	.539	1.00	1.331	.0315
113	1127	2.01	7.40	.259	.351	0.943	1.274	.0495
109	1128	2.10	7.73	.406	.538	1.36	1.759	.0431
110	1128	2.05	7.54	.409	.542	0.80	1.061	.0259
111	1128	2.06	7.58	.446	.580	1.69	2.236	.0508
115	1128	2.15	7.92	.263	.362	1.32	1.67	.0639
114	1129	2.13	7.84	.269	.373	1.05	1.345	.0503
147	1139	2.0	3.6	.206	.233	.392	1.09	.0525
148	1139	2.10	3.78	.205	.234	.482	1.27	.0629
149	1139	2.11	3.79	.207	.233	.360	0.95	.0456
129	1149	2.01	7.36	.222	.516	1.323	1.798	.0817
150	1151	2.25	4.05	.204	.233	.400	.987	.0487
151	1151	2.03	3.65	.206	.233	.560	1.534	.0750
152	1151	2.00	3.60	.208	.237	.532	1.479	.0708
169	1158	40.0	22.4	.457	.102	6.63	3.0	.0666

Experimental Results.

3. Toluene.

Toluene: Experimental results.

Section 2.

Run	T°K.	Time of run (mins) T	Moles of Toluene X 10^4	Time of Contact (secs) t	Partial pressure Toluene mms. Hg	Moles dibenzyl X 10^5	% dec^n.	k
4	1065°	6.0	34.5	0.742	1.26	0.12	0.30	0.0046
6	1097	5.5	31.6	0.609	1.53	0.19	0.63	0.0102
7	1100	5.0	28.8	0.506	0.96	0.11	0.38	0.0077
8	1108	5.0	28.8	0.557	1.07	0.14	0.48	0.0091
3	1131	5.1	29.4	0.424	0.85	0.52	1.77	0.0418
5	1140	6.0	34.5	0.783	1.44	0.75	2.10	0.0282
2	1173	5.0	28.7	0.396	1.82	0.74	2.59	0.0885

Section 3.

Run	Temp. (°K)	Time of run (min.)	Time of contact (sec.)	Moles Toluene x 10^4	Partial Press. Toluene (mms.Hg.)	Moles H_2 x 105	Moles CH_4 x 105	H_2/CH_4	% dec^n.	k.
42	1030	30.0	.122	88.3	0.99	0.112	0.033	3.4	0.016	0.0075
41	1049	30.6	.104	75.3	0.90	0.152	0.080	1.9	0.030	0.0026
43	1077	10.0	.323	44.0	0.53	0.016	0.068	0.24	0.020	0.0057
40	1117	9.0	.314	39.6	0.50	0.096	0.380	0.25	1.200	0.0374
10	1120	6.5	.798	37.3	1.80	0.150	0.210	0.71	0.960	0.0115
37	1122	6.0	.322	26.4	0.52	0.019	0.180	0.10	0.760	0.0222
38	1123	6.0	.311	26.4	0.49	0.024	0.120	0.20	0.530	0.0170
39	1129	6.0	.317	26.5	0.51	0.080	0.310	0.26	1.470	0.0414
3	1131	5.1	.424	29.4	0.85	0.160	0.320	0.50	1.630	0.0420
15	1140	4.3	.374	18.9	0.50	0.070	0.170	0.41	1.200	0.0314
5	1140	6.0	.783	34.5	1.44	0.260	0.460	0.56	2.050	0.0243
19	1140	4.2	.391	18.3	0.58	0.060	0.180	0.33	1.300	0.0324
16	1141	4.0	.361	17.6	0.54	0.030	0.150	0.20	1.200	0.0274
17	1141	4.1	.378	17.9	0.56	0.080	0.180	0.45	1.450	0.0365
18	1141	4.1	.381	18.2	0.56	0.050	0.150	0.33	1.100	0.0284
36	1147	6.0	.305	26.4	0.49	0.105	0.079	0.13	0.700	0.0218
35	1149	4.0	.306	17.6	0.51	0.024	0.145	0.35	0.960	0.0315
22	1159	4.0	.442	17.6	0.48	0.120	0.280	0.43	2.270	0.0509
20	1160	4.3	.400	18.7	0.55	0.102	0.312	0.33	2.190	0.0541
21	1160	4.2	.417	18.5	0.57	0.094	0.292	0.32	2.060	0.0474
33	1163	4.0	.298	17.6	0.50	0.086	0.235	0.37	1.820	0.0602
34	1163	4.0	.299	17.7	0.50	0.120	0.320	0.38	2.48	0.0778
30	1169	4.0	.307	17.6	0.51	0.100	0.280	0.36	2.16	0.0704
31	1171	4.0	.308	17.6	0.51	0.120	0.350	0.34	2.67	0.0845
32	1171	4.0	.304	17.6	0.51	0.090	0.281	0.32	2.10	0.0696
29	1175	4.0	.278	17.6	0.47	0.160	0.323	0.50	2.74	0.0984
23	1178	4.0	.426	17.6	0.58	0.103	0.454	0.23	3.16	0.0734
24	1178	4.0	.481	17.8	0.63	0.091	0.506	0.18	3.35	0.0693
26	1179	4.0	.537	17.6	0.72	0.065	0.488	0.13	3.14	0.0582
27	1179	4.0	.318	17.2	0.53	0.190	0.256	0.75	2.58	0.0816
28	1179	4.0	.313	17.6	0.53	0.180	0.268	0.67	2.54	0.0816

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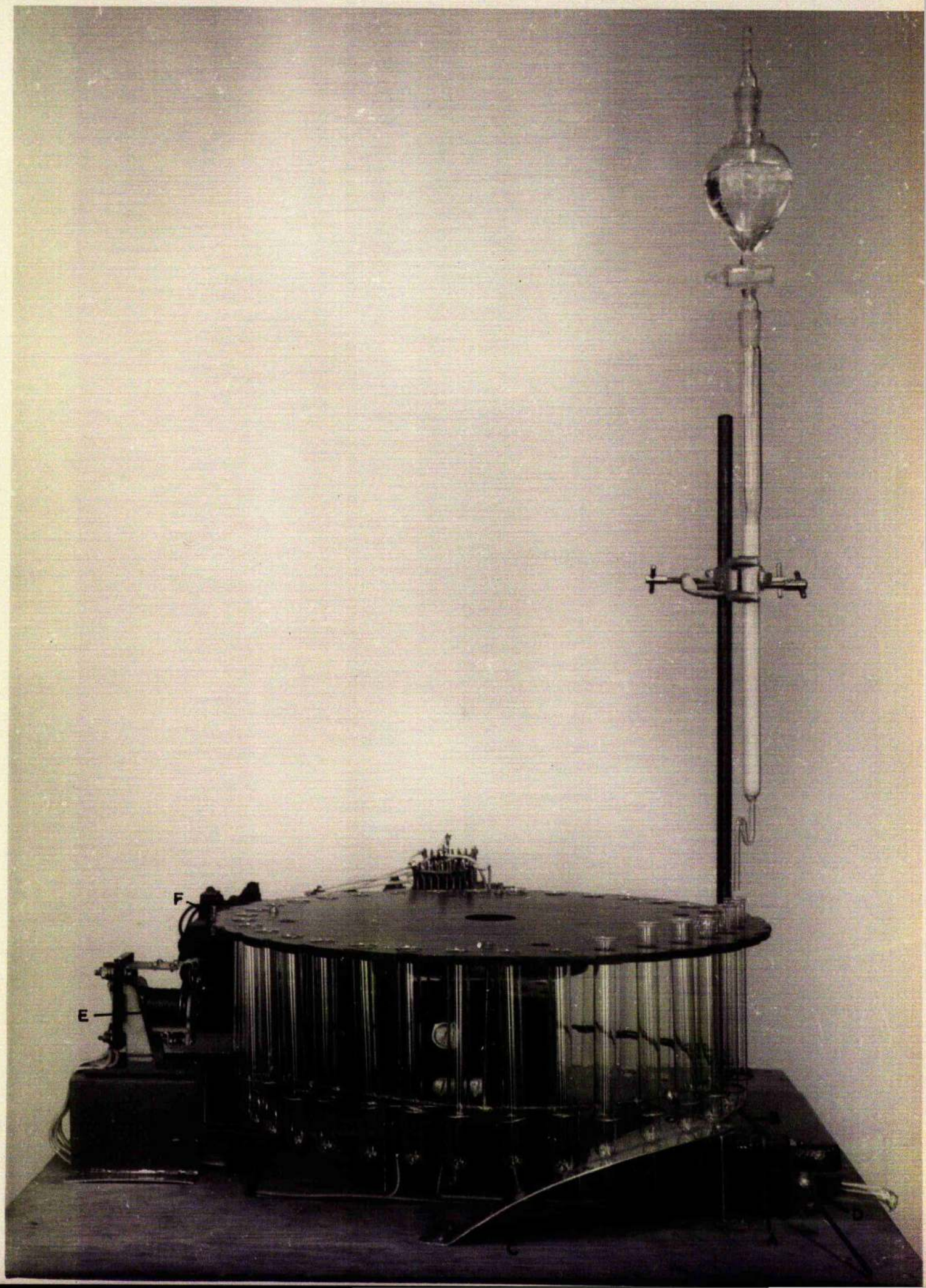
A P P E N D I X.

Constructional details of chromatographic fraction cutter.

As is seen in the photograph of the cutter the weight of the contents of a filled test tube was used to actuate the rotary mechanism. A standard micro switch (A) was modified by fitting brass side pieces to take a balance arm in the form of a 14" length of $\frac{1}{8}$" diameter silver steel rod (B). Each test tube, after rising up the aluminium ramp (C), rested on an aluminium cup fitted to one end of this balance arm, the other end carrying a brass counterpoise (D), the distance of which from the fulcrum was adjustable to control the amount of liquid collected.

24 volts D.C. was applied by the micro switch to a modified relay (E) which withdrew a detent finger (F) from a V cut on the periphery of a 17" diameter disc of Tufnol. The closing of the relay supplied current to a geared aircraft aerial winding motor which caused the Tufnol disc to rotate. As soon as the disc moved, the filled test tube left the button on the balance arm, disconnecting the relay energising current. In order to keep the disc rotating the relay contacts were kept closed mechanically by causing the detent finger to ride along a raised portion of the periphery of the disc. When the next empty tube fell on the aluminium cup, the detent finger had fallen into the next V cut of the disc, so stopping the motor.


F
E

A speed control for the motor was fitted so that the motor had just sufficient starting torque to commence rotation and enough inertia to cause the detent finger to engage firmly in each V of the disc.

The disc had 34 holes, each hole taking a $\frac{3}{8}$" test tube; selection of commercial test tubes being necessary to ensure that all "rode" freely in the holes.

The column shown in the photograph is fitted with a restricted flow device which, with a 250 mls. capacity tap funnel, enabled the cutter to operate for $2\frac{1}{2}$ hours without attention.